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MASTER

DEVELOPMENT OF RADIATIVE-COOLING MATERIALS

FINAL TECHNICAL REPORT: FY 1980-1981

DOE CONTRACT # DE-FC03-80SF11504

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FOREWARD

This final report was prepared by Energy Materials Research Company (EMRC) under a Department of Energy (DOE) research contract # DE-FC03-80SF11504 on the "Development of Radiative Cooling Materials." Research was conducted during the 14 month period 10/1/80 - 11/30/81 under FY '81 funding. Submittal of this report fulfills all the requirements for this contract.

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I. INTRODUCTION--PROGRAM GOALS AND OBJECTIVES

The work described involves research and development on glazing and selective emitter materials that will enhance day and night sky radiative cooling. It should be noted that our main emphasis was on glazing development with a secondary interest in development of the appropriate selective emitter. In addition, our work was oriented towards producing material(s) suitable for use in a wide range of configurations. Thus, our testing focuses on the individual material properties. System performance testing, which was beyond the scope of this work, should be done in a variety of acceptable configurations to ascertain each system's performance.

Both of the materials in question must have certain optical properties in order to allow radiative cooling. The glazing material must transmit infrared radiation between 8-13 microns while the selective emitter must be highly absorbing (and thus highly emitting) in that same region. For daytime cooling to be possible the glazing material should be highly reflective to the solar spectrum or, if the selective emitter is solar reflective, the glazing can be solar transparent. Polyethylene, the only glazing/binder material significantly transparent to 8-13 micron radiation, is amenable to either of two processes by which optical properties can be manipulated:

- 1) Deposition of optical thin films on glazing material or,
- 2) Introduction of pigments into the glazing matrix.

The compounding/extrusion production technique for the pigmentation of polymers was found to be far superior to the various methods of thin film deposition for the following reasons:

- 1) Firstly, film extrusion can accomodate pigment particles. A well designed technology of paints and pigmented plastics is easily accessible which eases material development in this area.
- 2) Secondly, film extrusion is inexpensive and rapid: Pigmented films cost about one tenth as much as vacuum coated films. Production speeds of film extruders are roughly 500

linear feet per minute, whereas vacuum sputtering machines run at 2-5 linear feet per minute.

- 3) Thirdly, there is an existing capital base of available extrusion equipment that can be accessed easily by rental, whereas vacuum production machines must be built individually for each application at a cost of one to two million dollars. This straight forward commercialization is the overall aim of this program and will eliminate many later tasks in subsequent phases.
- 4) Finally, many thin film coatings have severe corrosion problems and would necessitate encapsulation or some other life enhancement procedure over and above that necessary for the polymer itself.

The above process could also be used in the production of the selective emitter material and thus shows double promise in its applicability. In addition, other processes for selective emitter fabrication were entertained as many of the problems associated with applying optical films to plastic do not occur when working with substrates like aluminum foil.

In addition to the optical properties mentioned above, the materials must show an ability to resist corrosion over a long period of time (this pertains mainly to the glazing materials as they are most exposed to the elements). Only with this important quality will the created materials be of any long term use. The original objective of the present work was to achieve the necessary optical properties and then focus on the long range life enhancement properties. As our research progressed, we discovered that the longevity of the pigmented glazings were intimately connected with the pigmentation used. For these glazings then, the two sets of properties were addressed simultaneously.

Our tasks, then, included:

- 1) Complete definition of product performance goals.
- 2) Selection of selective emitter material and sample fabrication if time permitted.
- 3) Selection of the appropriate pigments and life enhancement additives for glazing and production of samples for optical and weather testing.

- 4) Test any samples produced and compare to the desired performance goals.

Each of these tasks is discussed in the section entitled Phase II Work.

Preceding the discussion of the above tasks is a short section on the background of radiative cooling (entitled Background). This section includes a brief discussion of the potential energy savings of, theoretical basis of, and previous research done on radiative cooling materials. It is designed for those less familiar with the field and therefore can be skipped without loss by those more familiar with current research on these materials.

II. BACKGROUND

II.1. Potential Energy Savings

It is critically important to develop low energy consuming cooling systems. According to the LBL Passive Cooling Group, 1.1×10^{15} BTU of energy were used in 1977 for residential space cooling. Twenty-four billion gallons of oil would be required to produce this much energy via a conventional fuel oil burning facility. According to the 1981 World Almanac, 133 billion gallons of oil were imported to the U.S. in 1977, so energy consumption for residential space cooling was approximately equivalent to 18% of U.S. oil imports.

Peak radiative cooling rates of 100 w/m^2 have been demonstrated at night, and rates of 50 w/m^2 have been reported during the day (see Previous Work section below). With practical materials and systems, we feel that average day/night rates of 60 w/m^2 can be realistically expected in most U.S. climates. We estimate that radiative cooling, in conjunction with thermal mass and conservation practice, can take over at least half of the residential cooling requirements. Thus, radiative cooling systems could replace up to the equivalent of 10% of U.S. oil imports. Industrial and commercial radiative cooling systems could add a large percentage to this savings.

Radiative cooling works best in hot dry climates. Gene Clark, however, has recently calculated that radiative surfaces reach the ambient wet bulb temperatures, even in coastal regions (1). If validated, this result puts ASHRAE comfort conditions within the reach of radiative cooling nearly everywhere in the U.S.

II.2. Theoretical Basis

II.2.A. General

The basis for selective radiative cooling is the spectral radiance of the atmosphere. Figure 1 shows the zenith atmospheric spectral radiance published in 1978 by Berdahl and Martin (2). Inspection of this figure shows that the radiance is depressed in the interval 8-13 microns compared to a black body. The magnitude of the depression correlates inversely with the amount of water vapor present. If a black body is placed on a horizontal surface at night, it will cool below ambient temperature because it initially emits more radiation than it absorbs. The difference is simply the difference in area under the black body curve and under the appropriate atmospheric radiance curve.

The first technique used to improve cooling performance over a black body is to develop a material that emits radiation only in the 8-13 micron interval (see figure 2). By Kirchhoff's law of selective radiation, this selective emitter material will be absorbing only in the same wavelength interval. If exposed in a dry climate, such a material will absorb only the depressed 8-13 micron radiation, while emitting at a high rate in the same interval. Another way of looking at this is to note that much of the radiation in the 8-13 micron interval originates from higher altitudes which are cooler. Figure 3 shows that much of the 8-13 micron radiation originates in the upper atmosphere (3).

The next technique for improving cooling performance is to use a glazing, which is similar in concept to glazings used to improve the performance of solar collectors. The primary difference is that one wants to trap a cool air layer for radiative cooling and a hot air layer in the case of a solar collector (see figure 4). The material requirements are significantly different because the glazing for cooling purposes must be transparent to 8-13 micron radiation, whereas a solar collector glazing should absorb or reflect infrared radiation to prevent heat loss.

FIGURE 1. Zenith Atmospheric Radiance of the Atmosphere

IDEAL REFLECTANCE CURVE FOR SELECTIVE EMITTER

FIGURE 2.

FIGURE 3. Height Origin of 8-13 Micron Radiation in Atmosphere

BASIC RCM

FIGURE 4. Radiative Cooling Device

II.2.B. Sensitivity Analysis for Glazing Transmission and Emitter Selectivity

The relative efficiencies of the emitter surface (i.e. degree of selectivity) and the glazing (i.e. degree of transparency to 8-13 micron radiation) strongly affect the performance of the device as a whole. Assuming a balance of IR flux that stagnates the emitter when it reaches the sky temperature, a decrease in glazing transmission, for example, will deteriorate both the cooling rate and stagnation T performance. Calculations of the cooling performance are simply handled by the method of Meinel and Mckenney (4). These equations include effects of surface selectivity, glazing IR transmission, laminar convective uptake, and sky emissivity. Figure 5 shows the results of these calculations as performed by Brookes and Blanpeid (see appendix A for calculation method). The climate ETIR is held constant at 0.6 black body between 8-13 microns, and 0.9 at other wavelengths in the sky emission. This results in a total ETIR fraction of about 0.8. The conditions chosen were rather adverse for radiative cooling but this yields similar results for other climates.

The analysis shows the advantage of high transmission glazings and a selective surface, (again figure 5). It also illustrates their interdependence. The ideal flat black (A) has a performance at $\Delta T = 7^{\circ} \text{C}$ comparable to the ideal selective surface (B). However, when the heat gain due to the IR emission from the glazing is taken into account, the selective surface configurations (C,D) for glazings with transmissions of 90% and 80% respectively, out perform their flat black counterparts by a wide margin. The main reason is that the selective surface is less sensitive to IR uptake from the glazing. In electrical filter terms, the selective surface has a higher Q, and therefore rejects unwanted heat better.

So far the discussion has focused on nighttime radiative cooling. A radiative cooling device exposed to solar radiation will decrease in performance as the solar heat uptake counteracts the developed ΔT . This solar uptake can be avoided by using a

FIGURE 5.

Sensitivity Analysis of Cooling Performance
vs. Glazing Optical Properties
($T_{amb} = 30^{\circ}\text{C}$, see text and appendix)

----- = selective surface
———— = flat black

solar reflective emitter or glazing material (this would be reflective to regions 1 and 2 in figure 6 while remaining either emitting or transparent to thermal infrared radiation depending on component). The final efficiency of the system depends on all these factors combined.

II.3. Summary Review of Previous Work in the Field of Radiative Cooling

As the emitter surface and glazing are the two critical elements to radiative cooling, previous research has focused on the development of these materials. The first discussion of selective infrared radiation cited in the literature is contained in a 1959 Australian patent by Head (5). He experimented with silicon monoxide on aluminum as a selective emitter. Improvements over typical black body cooling rates were demonstrated.

A more thorough investigation was performed in 1963-67 by F. Trombe, et al (6-9). They coated aluminum radiators with polyvinylchloride and used clear polyethylene as a glazing material. Using these devices in stages, temperatures nearly 40° C below ambient were achieved. The most significant improvements on Trombe's work were achieved in 1975-80 by the Italian group of Silvestrini et al (10-13), who used Tedlar instead of PVC as the selective emitter and experimented with pigmented polyethylene glazings to improve daytime cooling performance. With these glazings daytime cooling rates of 50 w/m² and nighttime rates of 100 w/ m² were reported. Less frequently cited studies have been performed in France (14, 15), Canada (16), Mexico (17), Chile (18, 19), Malta (20) and Australia (21-23).

FIGURE 6. Solar and 300° K Black Body Spectrum

III. PHASE II WORK

III.1. Product Performance Goals

In an effort to better characterize the materials needed for daytime radiative cooling, a variety of physical systems and their component parts were considered. The optical properties of these systems are below:

SYSTEM 1

- (a) UV protected (i.e. absorbing or reflecting UV for long lifetime) polyethylene top layer which reflects solar radiation and transmits thermal infrared radiation.
- (b) Selective emitter in the 8-13 micron range.

SYSTEM 2

- (a) UV protected polyethylene top layer which transmits solar and thermal infrared radiation.
- (b) Selective emitter in the 8-13 micron range while being highly reflective to solar radiation.

SYSTEM 3

- (a) Black (i.e. highly solar absorbing) polyethylene top layer which transmits thermal infrared.
- (b) Selective emitter in the 8-13 micron range.

Estimates of cooling (heat loss) for these systems were made using the calculation method described in sections II.2.B. and IV.1. while taking into account solar uptake of both glazing and selective emitter. System 3, while having the advantage of an extremely long lived glazing, showed little promise for daytime cooling (though could be use for nighttime cooling). Because our focus was on daytime cooling enhancement, this system was not developed further. Systems 1 and 2 showed equal promise and were pursued in tandem. For a complete outline of the materials' optical properties refer to figure 7 (24). The selective emitter for system 1 is listed as solar reflecting as this would enhance the solar heat rejection of this system.

In addition to these optical properties necessary for radiative cooling, other properties are necessary for utilization of these products as consumer items. For example, the glazing films must have both adequate mechanical and weathering properties for the suggested end use.

Reviewing thus far we see that three basic materials are needed to complete these systems:

- 1) Solar reflective, thermal infrared transparent, long life polyethylene glazing.
- 2) Solar transparent, thermal infrared transparent, long life polyethylene glazing.
- 3) Solar reflective, 8-13 micron selective emitter.

OPTICAL PROPERTIES
OF RCM SYSTEMS

	UV (.25 - .4 microns)	VISIBLE + NEAR-IR (.4 - 3.0 microns)	INFRARED (8 - 13 microns)	INFRARED (5-8/13-50 microns)
SYSTEM 1				
GLAZING	Absorbs transmittance < .01	Reflects reflectance > .95	Transmits transmittance > .90	Reflects
SELECTIVE EMITTER	n.a.	n.a.	Emits emittance > .90	Reflects reflectance > .90
SYSTEM 2				
GLAZING	Absorbs transmittance > .01	Transmits absorptance < .05	Transmits transmittance > .90	Transmits
SELECTIVE REFLECTOR	n.a.	Reflects reflectance > .95	Emits emittance > .90	Reflects reflectance > .90

FIGURE 7. Optical Properties of RCM Systems

III.2. Selective Emitter

III.2.A. General

Our search for a selective emitter began with an extensive survey of absorption spectra in hopes of finding a material with a near ideal absorption curve. Silicides, nitrides, borides, sulfides, and carbides were among the first materials investigated as their Restrahlen bands looked promising for emissivity in the 8-13 micron range. In addition to spectral criteria, the materials had to be environmentally durable and producable in a cost effective manner to be selected.

Over a thousand spectra were examined. The most promising materials were two previously studied compounds, polyvinylidene fluoride (Tedlar) and silicon monoxide, and two new candidates, silicon dioxide and silicon nitride. A description of each follows.

III.2.B. Candidate Materials

Tedlar is available in sheet (film) form from E.I. Dupont De Nemours & Co., Polymer Products Department, Wilmington, Delaware. The primary problem with Tedlar is that its absorption spectrum is different from the ideal. It begins absorbing at 6.5 microns instead of at 8.0 microns, and begins transmitting again at 12 instead of 13 microns (see figure 8). The absorption at 6.5 microns means that more heat will be absorbed from the atmosphere than is theoretically necessary. Likewise, the transmission at 12 microns means that the 8-13 micron 'window' is not being fully used for emission. Another less significant problem is absorption of thermal infrared radiation at 18-30 microns. There is not much atmospheric radiation in this interval, as at shorter wavelengths, but the pigments used for the reflective glazing absorb in this region. This means that the 18-30 micron radiation emitted by the Tedlar will be absorbed by the glazing, heating it, and limiting the system performance. This could

FIGURE 8. Infrared Transmission Spectrum of Tedlar

possibly be used to advantage to prevent condensation on the glazing, but is generally undesirable because cooling performance is decreased.

Silicon monoxide (SiO) has a very narrow absorption band at 10-12 microns, when prepared 1.0 micron thick. Problems with SiO are that the 10-12 micron absorption does not take full advantage of the 8-13 micron 'window,' and the absorption band is thickness sensitive (see figure 9)(25). Samples 1.2 microns thick show significant absorption between 13-18 microns. The experiments performed to date have used silicon monoxide prepared by vacuum evaporation. Vacuum evaporation processes are used commercially, but the associated costs add up to a dollar per square foot. When compared to approximately five cents per square foot for Tedlar, and about the same price for glazing material, a dollar or two per square foot is quite expensive. We therefore do not consider SiO to be a commercially practical product.

Silicon dioxide is a cheap, durable material. The primary problem is that it absorbs 8-11 microns instead of the 8-13 micron ideal. Silicon nitride is not as cheap as silicon dioxide, but it is relatively inexpensive and is extremely durable. It absorbs from approximately 9-15 microns. Since the silicon dioxide absorption cut-off was a little too soon (at 11 instead of 13 microns), and the silicon nitride cut-off was a little too late (at 15 instead of 13 microns), it seemed reasonable that a mixture might cut off at the desired 13 microns. This was investigated and absorption spectra published by Chu et al (26-27) show that a 5% silicon nitride, 95% silicon dioxide amorphous film (silicon oxynitride) has an almost ideal absorption spectrum (see figure 10).

The preparation method was discovered via Dr. Bruce Deal of Fairchild Semiconductor, who had previously prepared films of this type by chemical vapor deposition (CVD) (28). CVD is a relatively inexpensive commercial process so the constraint of production capability in a cost effective manner can be satisfied as well. Two production methods become immediately apparent:

FIGURE 9. Infrared Reflectance Spectrum of SiO

(Chu et al.) Infrared spectra of Si_3N_4 - SiO_2 amorphous films. (From

FIGURE 10.

- 1) CVD a SiO_xN_y film onto aluminum foil,
- or 2) compound SiO_xN_y powder into polyethylene, prepare film , and laminate to aluminum foil.

The aluminum foil is for solar reflection and low emission in the IR range. This allows the selective emitter material to be the dominant factor in this region. The actual selectivity of the SiO_xN_y can be optimized by careful selection of either film thickness (29) or particle size (30) depending on the method used. Doing this allows one to increase the emission slightly in the 8-13 micron range due to interference and scattering effects (though the majority of the selectivity is due to bulk material properties). Finally, we see that the silicon oxynitride system has better optical properties than the Tedlar as well as economic feasibility.

After the bulk of our selective emitter work was completed a report by Granqvist et al described the production of silicon nitride via electron beam evaporation for use as a selective emitter (see figure 11) (31). They noted that their sample was only mildly pure with a certain amount of oxygen contamination (silicon oxynitride?). This report lends considerable weight to the need to develop low cost methods of producing this material.

III.2.B. Aquisition of Material

Procuring a sample of the silicon oxynitride was even more difficult than finding the spectra and preparation method. We have as yet to locate a commercial source of the material though an exhaustive search has not been completed. We were able to obtain a small sample taken from one of the process reactors at Fairchild. Because the reactor was not set up for high purity production of silicon oxynitride, the level of contaminants (mostly ammonium hydroxide, NH_4OH) rendered useless our efforts to compound it into polyethylene.

Reflectance for Si₃N₄ + Al films.

FIGURE 11.

III.3. Glazing Research

III.3.A. General

As stated previously, the configurations identified in the product performance goals demanded the development of two different infrared transparent glazings: 1) one solar reflective, and 2) one solar transparent. The radiative cooling glazings are in general 2-4 mil polyethylene films which must withstand outdoor exposure. Polyethylene is used because it is one of the only known materials transparent to radiation in the 8-13 micron region. This creates, however, a difficult problem in polymer stabilization as it combines several features which lead to rapid degradation: 1) maximum surface area per unit mass, 2) UV, thermal, water, wind and corrosion exposure, and 3) polyethylene, a relatively short lifetime polymer. Thus, it is absolutely necessary to lengthen the lifetime of the glazings with stabilizers.

Our glazing work at EMRC, then, focused on two elements: 1) identification of polyethylene compatible IR transparent solar reflecting pigments, and 2) polyethylene lifetime stabilization. These elements were tackled via the following tasks:

- 1) an in-depth research program,
- 2) preparation of sample films,
- 3) testing of samples,
- and 4) small scale production of glazings.

The initial stage of our research was a careful literature survey of current means of polymer (specifically polyethylene) stabilization and solar reflecting pigments. This included seeking out data, spectra and developed theory from previous experimentation. In addition, and perhaps more important considering the rapidly advancing nature of these fields, experts in both the research and manufacturing arms of the plastic, stabilizer, and pigment industries were consulted. These technical resources were critical to our work as a free flow of information and

current technology developed.

After careful consideration, materials were selected and samples produced. Forty film samples of 11 different component variations were prepared. These samples were then submitted to a series of tests including: 1) infrared transmission, 2) transmission, reflection and absorption of the solar spectrum, 3) infrared emissivity, and 4) accelerated weather testing.

Finally, two glazing combinations (one transparent and one reflective) were selected for a small scale production run totalling 5000 sq ft. Large samples of these two glazings have been sent to a variety of research groups and individuals wishing to test the materials (see appendix V.2. for list). In addition, arrangements have already been made with Trident Energy Systems to test our materials in their Radiant Slab Cooling System.

The following three sections discuss polymer degradation/stabilization, solar reflecting pigments, and the formulations prepared respectively. Because the presence of pigments in the polymer mixture effect the action of certain stabilizers, enhancement of the reflective glazing lifetime became a problem separate from that of the solar transparent glazing. The basic concepts of polymer stabilization, however, apply equally well to both glazing types.

III.3.B Polymer Degradation/Stabilization

Process Description

The mode of degradation of polyethylene is primarily auto-oxidation, a free-radical chain propagation process. The environmental causes of this degradation are UV radiation and thermal excitation. UV oxidation does not begin on the aliphatic polyethylene chain itself, but rather at carbonyl groups inadvertently introduced in the processing and preparation of the polymer (32). Absorption of UV produces an electronically excited species, which decomposes and is quenched by oxygen, leading to the formation of hydroperoxide and further free-radical chain propagation (33). Thermal oxidation is an auto-

cataytic process in which the primary product of the reaction is the formation of a hydroperoxide which decomposes to form free radicals which initiate the chain reaction (34).

There are several ways in which UV and thermal oxidation processes can be inhibited (see figure 12): A) UV absorbers, B) excited-state quenchers, C) hydroperoxide decomposers, and D) anti-oxidants, for free-radical chain termination. In general, more than one of these approaches is used and sometimes more than one chemical for each approach. However, problems of compatibility, cost, and interactions between stabilizers usually mean that no more than three additives are used.

Non Polymeric Additives

A. UV Absorbers. The state-of-the-art for UV absorbers in polyethylene are the 2-hydroxy-4-n-alkoxybenzophenones and substituted benzotriazoles. These absorbers contain an intramolecular hydrogen bond, which converts the absorbed UV radiation into vibrational energy by radiationless routes without a change in spin multiplicity (internal conversion) (35). Among the benzophenones, we are examining Ferro AM-320 and Cyasorb UV-531; and among the benzotriazoles, Tinuvin 328.

B. Quenchers. Quenchers remove energy from the excited state of the polymer, after UV radiation has been absorbed, and convert it to vibrational or non-UV radiation. We are studying two classes of quenchers: thiobisphenol nickel chelates and hindered amines. The nickel chelates we are using include Ferro AM-105 and Cyasorb UV-1084. Hindered amines are a new class of quencher currently available only from Ciba-Geigy. They appear to stabilize against photodegradation by a variety of mechanisms, including the quenching of excited state oxygen. The monomeric form is Tinuvin 770. An oligomer is also manufactured, Chimasorb 944, which is preferred for LDPE (low-density polyethylene).

C. Hydroperoxide Decomposers. Hydroperoxide decomposers destroy the primary product of thermal oxidation, preventing the initiation of free-radical chain propagation (36). Thus, they are preventive anti-oxidants. Salts of N,N-disubstituted dithio-

POLYETHYLENE DEGRADATION PATHS

FIGURE 12.

carbamates, such as Ferro AM-104 which is a nickel salt, destroy hydroperoxides. However, it imparts a deep color to polyolefins which makes it inapplicable for the solar transparent glazing. It may, however, be worth testing for the solar reflective glazing.

D. Chain-Breaking Anti-Oxidants. A wide variety of chemical classes provide effective inhibition of free-radical chain propagation (37). We are examining Naugard-P, an aromatic phosphite ester from Uniroyal, especially recommended for use in transparent polyethylene because of its non-yellowing characteristics over long periods of time. Other classes of chain-breakers that are worth studying include hindered phenols, thiobisphenols, and fatty acid dithiopropionates. The hindered phenols act as hydrogen radical donors (38). Ralph Hickcox, a well known plastics consultant, recommended hindered phenols as the antioxidant of choice with emphasis on Irganox 1010 (from Ciba-Geigy). It should be noted that carbon black acts as a very effective chain-breaking anti-oxidant in polyethylene, forming stabilized aromatic and quinone radicals (39). We are also examining Ferro AM-340, an anti-oxidant recommended by Ferro Corp.

III.3.C. Solar Reflecting Pigments

To reflect the solar visible region, the material must appear white. A high index of refraction is required for good white opaque pigments (40). Other important criteria include IR transparency in the 8-13 micron range and economic and mechanical feasibility. The absorption spectra of the economically and mechanically feasible materials were located and considered (some materials are mechanically infeasible because they do not disperse well into polyethylene). Many candidates were found in tables of white pigments used in the paint industry (41). Several of the candidates reviewed are listed below:

Rutile Titanium Dioxide
Anastase Titanium Dioxide
Zinc Sulfide
Lithophone
Zinc Oxide
Basic Carbonate White Lead
Zinc Titanate

Of the candidates considered, the only solar reflecting materials with the proper 8-13 micron transparency were zinc oxide (ZnO), zinc sulfide (ZnS), and zinc titanate (ZnTiO_3) (see figures 13-15). ZnO , a UV absorber, was selected as the optimum pigment because of its polymer life enhancement properties (ZnO prepared by the ultra pure 'French Process' exhibited the best polymer life enhancement properties). These later properties are absent in the ZnS and unknown in the ZnTiO_3 .

In addition, a variety of life enhancement additives act synergistically to further improve ZnO pigmented film. These synergists, when used in combination with ZnO , prolong the film lifetime to a much greater degree than either material used alone. Infrared transparency testing revealed better performance by nickel complexes such as Ferro AM-105 which absorb less in the 8-13 micron range than by other synergistic compounds like Polygard, and Methyl Zimate (see spectra #1-3 of samples #1-3 in III.5.B. Optical Testing). Fortunately these nickel complexes are the synergists reported to produce the longest outdoor lifetime (42).

III.3.D. Formulation Choices

Due to the complexity of additive interactions (eg. synergistic activity) theoretical predictions of resultant formulaion ranking is difficult. The combinations evaluated or being evaluated thus represent our 'best guess' for optimum results. We based the choice of formulations on the following sources of information:

FIGURE 13. Infrared Transmission Spectrum of ZnO

FIGURE 14. Infrared Transmission Spectrum of ZnS

FIGURE 15. Infrared Transmission Spectrum of ZnTiO_3

- 1) Manufacturers suggestions
- 2) Plastics experts' suggestions
- 3) Previous weathering data taken
- 4) Spectral characteristics (when known)
- 5) Consideration of functional mechanism (when known)

The following three tables (tables I, II, III) list the various materials used in our experiments, the function of each additive used, and, the formulations used, the method of sample fabrication, and the type of spectra taken. These tables will be referred to throughout the rest of the report. The spectra listed appear on pages 43-65 (III.5.B. Optical Testing section).

Table I--Materials and Procedure Key

<u>Additives</u>	<u>Source</u>
A Zinc oxide	G+W Natural Resources
B Methyl Zimate	R.T. Vanderbilt Co.
C AM-105	Ferro Corp., Chem. Div.
D AM-320	"
E AM-340	"
F UV-531	American Cyanimide
G UV-1084	"
H Chimassorb 944	Ciba Geigy, Add. Div.
I Irgnaox 1010	"
J Tinuvin 328	"
K Naugard P	Uniroyal
L Polygard	"

Polyethylene Resins

R DYNH-1	Union Carbide
S 3220 F05	Arco
T NA 344--Barefoot	USI

Compounding and Film Production

V Compounded (Two-Roll Mill), Pressed ($6.0 \pm .5$ mils)
W Compounded (Brabender Mixer), Pressed ($2.5 \pm .5$ mils)
X Compounded (Banbury Mill), Blown Film ($2.0 \pm .1$ mils)
Y Compounded (Extruder), Blown Film ($2.0 \pm .1$ mils)
Z Compounded (Extruder), Blown Film ($6.0 \pm .1$ mils)

Spectra

TIR Spectral Thermal-Infrared Transmission/Absorption
SOL Spectral Solar Transmission/Absorption
DIF Diffuse Solar Transmission/Absorption and Reflection, Diffuse Thermal-Infrared Emission

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Table II--Additive Characterization

<u>I.D.</u>	<u>Protective Mechanism</u>	<u>Chemical Family</u>
A	UV Absorber	Metal Oxide Pigment
B	Antioxidant	Zinc Thiocarbamate
C	Quencher	Nickel Chelate
D	UV Absorber	Benzophenone
E	Antioxidant	Hydroxybenzoate
F	UV Absorber	Benzophenone
G	Quencher	Nickel Chelate
H	Quencher	Hindered Amine Oligomer
I	Antioxidant	Hindered Phenol
J	Quencher	Hindered Amine
K	Antioxidant	Aromatic Phosphite Ester
L	Antioxidant	Organic Phosphite

Table III--Formulation List

<u>No.</u>	<u>Additives (% by weight)</u>	<u>Resin</u>	<u>Other</u>	<u>Spectra</u>
0	NONE	R	V	TIR
1	A-6.0%, B-1.0%	R	V	TIR
2	A-6.0%, L-1.0%	R	V	TIR
3	A-6.0%, C-1.0%	R	V	TIR
4	A-8.0%, C-0.50%	S	W	TIR, DIF
5	A-8.0%, G-0.50%	S	W	TIR, DIF
6	A-8.0%, G-0.50%	T	X	TIR
7	H-0.25%, K-0.25%	S	W	TIR
8	F-0.30%, H-0.10%, K-0.20%	S	W	TIR
9	F-0.30%, H-0.10%, K-0.20%	T	Y	TIR, SOL
10	F-0.30%, H-0.10%, K-0.20%	T	Z	TIR, SOL
11	F-0.50%, G-1.0%	S	W	TIR
12	C-0.50%, D-0.75%, E-0.25%	S	W	TIR
13	H-0.25%	S	W	TIR
14	I-0.25%, J-0.25%	S	W	TIR

III.4. Sample Preparation

III.4.A. Process Description

There are two processes key to the production of polyethylene film, 1) compounding and 2) film preparation. The following is a brief discussion of each.

Compounding. Proper mixing is essential to uniform film performance irregardless of additive purpose. Though many methods are available for polyethylene compounding, the best method is somewhat dependent on the additives involved. Relative to compounding, additives can be placed into two categories:

- 1) Those that are 'soluble' in hot polyethylene. It is perhaps stretching it to refer to anything as 'soluble' in polyethylene, but those additives that are soluble in aromatic and other hydrocarbon solvents are much easier to disperse into the plastic than those that are not. (eg. most organic stabilizers are in this class).
- 2) Those additives that are merely dispersed into polyethylene. (eg. metallic oxides, sulfides, etc. are in this class).

The latter group of additives needs more intensive mixing to produce uniform dispersion. Unfortunately, application of a longer mixing time creates a problem of its own. The heat necessary in all polyethylene compounding accelerates the inevitable degradation process. Thus, the residence time and temperature must be kept to a minimum while retaining good mixing.

The devices currently available for such 'high intensity' mixing are:

Twin Screw Extruder--typically large

Banbury Mill-----typically large

Two Roll Mill-----lab sized models available

Brabender Mixer-----lab sized models available

A long single screw extruder is acceptable for the first class of

additives given a good premix.

Film Preparation. Some film properties are directly dependent on the film preparation technique utilized. The differences in properties (eg. weathering) are derived mainly from changes in the polyethylene chain orientation. There are three basic orientation types:

- 1) Amorphous or no orientation--obtained with heated high pressure press.
- 2) Unidirectional orientation--obtained through certain extruder dies.
- 3) Bidirectional orientation--obtained via blown film extrusion.

It has been shown that orientations #1 and #3 have similar properties (43). Most large scale thin film production of polyethylene is produced via the blown film method and thus laboratory samples were produced with a heated high pressure press.

III.4.B. Procedure and Equipment Employed

As opposed to purchasing the necessary equipment (a small lab-sized Brabender mixer costs \$15,000 alone), apparatus was leased or borrowed when possible.

Small Samples. The first four samples were prepared using a two-roll mill and heated press. Compounding of samples #4, 5, 7, 8, and 11-14 was performed in a 50 cc capacity Brabender mixer with final films made on a 100,000 lb/5 inch plunger hydraulic press. Clean highly polished ferro type plates were used in the presses to obtain high gloss films. A simple procedure outline for the second set follows:

- 1) Master batches of each additive were prepared by adding enough additive to the polyethylene resin to bring final additive concentration up to 12.5%.(*) Nine master batches were prepared.
- 2) Each master batch was pressed into a sheet about a

millimeter thick for easy handling.

- 3) Samples of each formulation were prepared by adding the appropriate amount of the master batches to raw polyethylene and mixing.
- 4) Each formulation was pressed into a sheet about a millimeter thick for easy handling.
- 5) About three grams of each formulation was taken and pressed to a film of between 2 and 3 mils for testing.

* The master batch containing Irganox behaved poorly due to it exceeding its maximum compatibility in polyethylene.

Compounding was performed at 320°F. Master and formulation batches were pressed for 15 seconds at 350°F while final films were pressed for 1-2 minutes at a pressure of 10,000 psi and a temperature of 350°F.

Production Run. Sample #6 was compounded in a Banbury mill for one minute at 350°F. The two clear samples #9 and 10 were put twice through a 2.5 inch Akron 24:1 single screw extruder at 335°F. The rate was 100 lbs/ hour. We were advised by plastic experts that a low temperature during mixing allows a second heat history without much increased degradation. It should be noted, however, that once through a 32:1 or larger ratio extruder or through a Banbury mill would give good quality mixing with less heat history.

All three samples were put through a 2.5 inch 24:1, 75 horsepower extruder with barrier screw (Keneer mixer). The die was 8 inches with a .032 inch gap. The films are four feet wide and 2 or 6 mils thick.

III.4.C. Future Methodological Improvements

It has become clear as our research progressed that the polyethylene degradation was extremely sensitive to the sample preparation method. In order to limit the number of variables we plan to use only the Brabender mixer as small sample compounder, and only one heated press for fabricating future films. Blown

film runs will all be compounded in a Banbury mill, passed once through pellitizer and then blown into film. The concentration of additive in the master batches will be decreased to avoid the limit of compatibility. Finally, one resin type will be used in all future samples.

III.5. Sample Testing

III.5.A. Introduction

The purpose of this task was to examine the properties of the newly prepared glazing samples and to compare these results with the goals developed in task I.A. The properties examined were two in nature:

- 1) transmission, reflection, absorption, and/or emission of radiation in the solar and/or far infrared wavelength ranges,
- and 2) accelerated weather testing.

The optical measurements were relatively straight forward whereas interpretation of the weather tests was considerably more difficult. Both are discussed in detail below.

III.5.B. Optical

Introduction

The optical performance goals are laid out in Figure 7 (section III.1. Product Performance Goals). Both glazing types were tested for their thermal-infrared (TIR, 2.5-50 microns) transmission/absorption and solar (.28-2.0 microns) transmission/absorption while only the reflective glazing type was tested for solar reflection. In general the life enhancement additives introduced little or no color to the polyethylene and thus the visible (VIS, .4-.7 microns) and near-infrared (NIR, .7-2.0 microns) radiation properties of each additive combination (within a glazing type) were assumed to be similar. When considered alone, the amount of ultraviolet (UV, .28-.4 microns) radiation absorbed gives little direct information about the weathering ability of the clear plastic and was thus only measured in one sample case. As final glazing compositions are chosen, complete spectral analyses will be performed.

Procedures and Instruments Employed

The following paragraphs briefly discuss the special techniques necessary for the measurement of sample glazing spectra. Topics include: 1) spectra of light scattering materials, 2) relationship between real and test radiation environments, 3) reflectance and emittance measurements of semi-transparent materials, and 4) the instruments used.

When measuring the transmission/absorption of a material one must be aware of radiation scattering due to sample particle size being comparable to radiation wavelength. For measurements of TIR this is rarely a problem and the present case is no exception. Thus, 'spectral' TIR measurements are sufficient. While a 'spectral' measurement of the solar spectrum (UV, VIS, and NIR) is sufficient for the clear glazing type, pigmented polyethylene is not analyzable via this technique. Scattering of radiation demands the use of special attachments to measure the 'diffuse' spectra.

A second factor influencing the interpretation of a spectrum is the range of intensities of the radiation incident on the material in its normal operating environment relative to that in the testing environment. In order to compensate for the variance in intensity of the solar spectrum over wavelength, measurements have been integrated relative to the 'Johnson Solar Curve.' This means that the 100% line at any wavelength is taken as the intensity of the sun's radiation incident on the earth at that wavelength. Unfortunately this is not the only factor influencing the intensity of solar radiation. Another factor is the presence of the atmosphere and how, with the relative movement of the sun, different thicknesses of air must be traversed. This creates an intensity function dependent on the position of the sun. A value of 'air mass 2' (which means essentially two atmospheric thicknesses) was chosen as a good approximation of the average value during the central part of the daylight hours (the solar intensity function varies with season and latitude as well as time of day).

Finally, one must consider the method of taking the

reflectance or emission spectrum of a semi-transparent material (i.e. reflective glazing). To measure the front surface or film reflectance one must use a black or highly absorbing backing material. This ensures that upon passing through the film once, no radiation is reflected from the backing surface, transmitted back through the film, and added to the radiation reflecting from the film itself. If, however, one uses a highly reflecting surface as the backing material, the total reflectance measured will be that of the backing/film system with the difference from one being the film absorption. ($ABS_{film} = 1 - REFL_{sys}$). An example of such a system is the solar reflective glazing/solar reflective selective emitter. In a similar fashion one can show how the emissivity of the backing material is important in the measurement of TIR emissivity. For the purposes of this task, emissivity measurements were made with black backings while both types of reflectance systems were measured.

The instruments utilized to obtain the spectra are listed below:

Perkins-Elmer IR Spectrophotometer Model 283
Spectral TIR Transmission/Absorption

Gier Dunkle Infrared Reflectometer Model DB 100
Room Temperature TIR Emission

Cary Spectrophotometer Model 14
Spectral UV, VIS, NIR Transmission/Absorption

Cary Model 17D with Integrating Reflectance Attachment
Diffuse Solar Transmission/Absorption and Reflection

Results

The following spectra are those listed in table III (section III.3.D. Final Formulation Choices of Glazing Material) in the following order:

Spectra 0-14 are the spectral TIR transmission/absorption spectra of samples 0-14 (But not in numerical order according to sample. See text below).

Spectra 15 & 16 are the spectral solar transmission spectra of samples 9 & 10.

Spectra 17-22 are the diffuse solar transmission, absorption and reflection spectra of samples 4 & 5.

Table IV is a listing of the integrated values of the diffuse transmission, absorption, reflection, and emission measurements of samples 4 & 5.

SPECTRUM 0. Original Infrared Transmission Spectrum--Sample 0

SPECTRUM 1. Original Infrared Transmission Spectrum--Sample 1

SPECTRUM 2. Original Infrared Transmission Spectrum--Sample 2

SPECTRUM 3. Original Infrared Transmission Spectrum-- Sample 3

SPECTRUM 4. Original Infrared Transmission Spectrum--Sample 4

SPECTRUM 5. Original Infrared Transmission Spectrum--Sample 5

SPECTRUM 6. Original Infrared Transmission Spectrum--Sample 7

SPECTRUM 7. Original Infrared Transmission Spectrum--Sample 8

SPECTRUM 8. Original Infrared Transmission Spectrum--Sample 11

SPECTRUM 9. Original Infrared Transmission Spectrum--Sample 12

SPECTRUM 10. Original Infrared Transmission Spectrum--Sample 13

SPECTRUM 11. Original Infrared Transmission Spectrum--Sample 14

SPECTRUM 12. Original Infrared Transmission Spectrum--Sample 6

SPECTRUM 13. Original Infrared Transmission Spectrum--Sample 9

SPECTRUM 14. Original Infrared Transmission Spectrum--Sample 10

SPECTRUM 15. Spectral Solar Transmission
--Sample 9

SPECTRUM 16. Spectral Solar Transmission
--Sample 10

SPECTRUM 17. Diffuse Solar Transmission--Sample 4

x-axis = wavelength in microns

y-axis = % trasmission, top of scale is 0%

SPECTRUM 18. Diffuse Solar Transmission--Sample 5
 x-axis = wavelength in microns
 y-axis = % transmission, top of scale is 0%

SPECTRUM 19. Diffuse Solar Reflection/Black Backing--Sample 4
 x-axis = wavelength in microns
 y-axis = reflectance, top of scale is zero

SPECTRUM 20. Diffuse Solar Reflection/Black Backing--Sample 5
 x-axis = wavelength in microns
 y-axis = reflectance, top of scale is zero

SPECTRUM 21. Diffuse Solar Reflection/Reflective Backing--Sample 4
 x-axis = wavelength in microns
 y-axis = reflectance, top of scale is zero

SPECTRUM 22. Diffuse Solar Reflection/Reflective Backing--Sample 5
 x-axis = wavelength in microns
 y-axis = reflectance, top of scale is zero

Table IV-- Integrated Values For Diffuse Spectra

<u>No.</u>	<u>Solar Trans.</u>	<u>Solar Absor.</u> <u>Black</u>	<u>Refl.</u>	<u>Solar Refl.</u> <u>Black</u>	<u>Refl.</u>	<u>TIR Emis.</u> <u>Black</u>
4	0.644	0.761	0.128	0.239	0.872	0.855
5	0.676	0.783	0.120	0.217	0.880	0.851

Solar Refl. = 1 - Solar Absor.

Solar Trans. + Solar Absor. (refl.) + Solar Refl. (black) = 1

Discussion

The following discussion will be broken down into three areas corresponding to the three types of spectra: spectral TIR, spectral solar, and diffuse solar. The three different 'sets' of samples to which the text refers correspond to the V, W, & X-Y-Z categories listed in table III. Lastly a comparison will be made between the original performance goals and the attained results.

Spectral TIR

Spectrum 0 is the spectrum of a $6.0 \pm .5$ mil sample of Union Carbide's DYNH-1 polyethylene resin with no additives. Note typical alkane absorption bands (all branched LDPE resins have approximately the same initial spectrum). The area of particular interest is the 8-13 micron atmospheric window. For polyethylene we see no particular structure in this region but there does exist a considerable amount of undesirable background absorption. Approximately 10% of this can be attributed not to absorption but to surface interference reflection due to index of refraction mismatch (5% per interface). The remaining background in this region is of unknown origin (A study of this affect would greatly enhance efforts in this field as certain modifications in the polyethylene may be able to decrease its intensity). It is this background absorption that demands the use of very thin films of polyethylene for radiative cooling (see spectra 9 & 10 for a comparison of 2.0 and 6.0 mil polyethylene films of the same composition).

The first set of samples (1-3; spectra 1-3) contained ZnO and a synergist at $6.0 \pm .5$ mil. Aside from the ZnO absorption band between 17-30 microns there are various spectral differences which cannot be rationalized by the thickness uncertainties. Specifically, we note that in both samples 1 and 2 there is a certain amount of structure (different from pure polyethylene) in the 8-13 micron range whereas sample 3 has no such structure. Optically, then, Ferro AM-105 (sample 3) is the synergist of choice (particularly when one realizes that normal concentrations of the AM-105 run around 0.5% as opposed to the 1.0% used

in this case).

The second set of samples (4, 5, 7, 8, & 11-14; spectra 4-11) contained a variety of additives at $2.5 \pm .5$ mil. The decrease in background absorption in the 8-13 micron range is significant though still not entirely satisfactory (refer to figure 7). Because there was no evidence of significant absorption in the 8-13 micron range due to additives, none were eliminated for these considerations.

The final set of samples (6, 9, & 10; spectra 12-14) are the blown film versions of two of the compositions in the second set (6 at $2.0 \pm .1$ mil and 9 & 10 at 2.0 and $6.0 \pm .1$ mil respectively. One can easily see the decreased background absorption in the 8-13 micron range as well as all over the TIR range in the 2.0 mil samples. The average transmission is about 83% which is sufficient for the purposes of radiative cooling.

Spectral Solar

Spectra 15 and 16 are the spectral UV, VIS, and NIR measurements of samples 9 and 10 (clear formulations of 2.0 and 6.0 mils thick). They show a high transparency to NIR and VIS radiation with a high absorption of UV radiation the latter of which is thickness sensitive. The small percentage of radiation (.05-.10 Abs.; 10%-20% T) in the VIS and NIR ranges that is not allowed to pass is partially from the surface interference reflection due to refractive index mismatch while the rest is due to surface irregularities introduced during the blown film process. These surface irregularities diffuse a small portion of the light such that error is introduced into spectral measurements. As to the UV absorption, we see that the 2.0 mil sample (of this formulation only) is not entirely opaque while the 6.0 mil sample is over 90% opaque.

Diffuse Solar

Spectra 17-22 are the diffuse solar transmission and reflection measurements of samples 4 and 5. Firstly we see that the two samples are nearly identical which is expected. The

front surface reflectance (reflectance with black backing) bears out the fact that the ZnO pigment used was engineered for VIS transmission...not absorption. From the system reflectance curve (reflectance with reflective backing) we note the true areas of absorption--which exist mainly in the UV range with some of the same structures as in the spectral solar measurements in the NIR range. The integrated values in table IV give the overall picture of the films' properties. The front surface solar reflection was between 21-24%, the solar absorption was between 12-13% and the solar transmission was between 64-68%. Because the blown film samples are a little thinner than the samples from set 3, the values of reflectance and absorption will decrease slightly with a corresponding increase in transmission. The emissivity measurements give a rough indication of the total TIR emission of the film at room temperature. This is important in calculating the glazing efficiency.

Summary

From the TIR measurements we see that to achieve better than 80% transmission in the 8-13 micron range films of at most 2.0 mils can be used. Unfortunately films of less than 2.0 mils (i.e. higher transmission) have little structural strength and thus become infeasible in most, but not necessarily all, applications. The solar transparency (NIR and VIS portions) of the clear films appears to be satisfactory with diffuse measurements necessary on rough films. The solar reflectivities of the white films are far from ideal.

III.5.C. Weather Testing

Introduction

Obviously the longest lived glazing material is desired as fewer replacement costs would be incurred. To expedite the process of lifetime determination accelerated weather testing was performed. Unfortunately, accurate correlations between laboratory accelerated weather tests and outdoor weather tests do not exist (44). Thus, it is extremely difficult to answer the common question 'How many years will this material last?' One can, however, achieve accurate ranking of the weatherability of most materials if care is taken to simulate the pertinent environmental conditions (45).

In this case we focus on 'photodegradation' resulting from polymer absorption of ultraviolet radiation. Other factors also important in polymer degradation are temperature and water exposure. The following sections describe the apparatus utilized, the results obtained, and some improvements to be made in future experiments.

Procedures and Instruments Employed

The photodegradative processes of most polymers occur below 0.35 microns with polyethylene being most sensitive to radiation around 0.30 microns (46, 47). In addition, because of the filtering properties of the atmosphere, little radiation below 0.29 microns is incident on the earth. It is critical then, to utilize a light source that is specific to this range. We chose the General Electric Company RS-4 Sunlamp for our tests on the basis of its spectral qualities (see table 5) and previous successful utilization of this bulb (48-50). Our test apparatus was modeled after the Sunlighter, a product of the Test-Lab Apparatus Company in Milford, NH, with certain modifications. The device was constructed in-house for reasons of cost.

Figure (16) shows a basic schematic of the weathering device. The samples are mounted on an aluminum disc 6.5 inches

Table V--100 Watt GE RS-4 Sunlamp Specifications

<u>Continuous</u> <u>Nanometers</u>	<u>Spectrum</u> <u>W/10nm/Lum.*</u>	<u>Line Spectrum</u> <u>Nanometers</u>	<u>W/10nm/Lum.*</u>
280	-----	-----	-----
290	3.3	296.7	69.3
300	26.6	302.2	131.4
310	67.5	313.2	407.0
320	79.6		
330	68.3	334.1	61.7
340	69.3		
350	80.3		
360	79.9	365.0	1118.7
370	56.6		
380	32.8		
390	23.7		
400	31.4	404.7	264.6
410	29.9		
420	21.9		
430	22.6	435.8	521.9
440	29.9		
450	21.9		
460	11.7		
470	9.1		
480	10.9		
490	10.9	491.6	7.3
500	10.2		
510	10.2		
520	10.9		
530	14.6		
540	21.9	546.1	669.8
550	27.4		
560	27.4		
570	23.7	578.0	571.2
580	23.0		
590	21.9		
600	14.6		
610	14.6		
620	14.6		
630	14.6		
640	14.6		
650	14.6		
660	14.6		
670	14.6		
680	14.6		
690	14.6	693.8	3.6
700	14.6		
710	14.6		
720	14.6		
730	14.6		
740	14.6		
750	14.6		

* W/10nm/Lum.=micro watts/ 10 nanometers/ Lumen

FIGURE 16

ACCELERATED WEATHERING DEVICE

below the focus of the three outboard sunlamp bulbs. The disc rotates at approximately 33 rpm. Mounted between the lamps and the samples are large pyrex evaporating dishes for low UV filtering as suggested by other researchers (51). Pyrex glass is opaque to UV radiation below 0.29 microns and thus acts as an excellent filter to ensure that nonsolar wavelengths are not transmitted to the samples. By absorbing considerable amounts of all UV radiation, these filters significantly reduce the accelerating factor. During these experiments all 4 bulbs were used and resulted in a temperature of approximately 60° C (140° F) (The forced air blower operating continuously). Bulbs were changed every 1000 hours.

The definition of sample 'failure' must now be considered. Three sets of properties are important for our purposes: 1) structural, 2) solar transmission or reflection, and 3) 8-13 micron transmission. Significant degradation of any of these properties is defined here as 'failure.' In general, it was found that the 8-13 micron transmission degraded (i.e. range became absorptive) before significant degradation of the other properties.

To assign an 'improvement factor' (the number of times a stabilized sample lasts compared to the control) we must define the exact time at which the spectral 'failure' occurs. This is difficult as the degradation mode is gradual over time. One must also be careful not to rely wholly on an average figure for transmission in the 8-13 micron region because: 1) there is a significant gradient in the energy from one end of the range to the other (photons emitted at 8.0 microns have approximately 1.5 times the energy as those emitted at 13 microns), and 2) degradation progresses with a distinct slope in that region, unfortunately with the higher energy wavelengths degrading first. With these considerations in mind we will define spectral failure as the point when the average percent transmission in the range 8-10 microns has decreased by 20% transmission. We monitored the entire infrared range by spectroscopy measurements.

One last consideration is the affect of sample thickness on

weatherability. Radiation induced polymer degradation begins as a surface reaction and then penetrates into the bulk of the material. Significant degradation of the surface can occur (e.g. discoloration, clouding, etc.) without much affect on the bulk physical properties (52). Because the 8-13 micron degradation in general occurs well before physical degradation it is probably limited to the surface (of course there is a limiting case where a sample is so thin that it will behave like a surface with no bulk). For this reason the use of a 6.0 mil control is sufficient for comparison with several sample thicknesses (2.0-6.0 mil).

Results

The first set of samples (#0-3) were exposed for approximately 1000 hours before infrared monitoring was commenced. At that time the next set of samples (#4-14, with another #0) was begun while the first set continued. Infrared monitoring was begun at this second loading of samples and was repeated approximately every 150 hours. Included in this section of results will be the last spectrum taken of those samples with essentially no degradation, and a series of spectra demonstrating the degradation process of each sample which exhibited signs of degradation in the given time period. A list of spectra follows:

Samples showing no degradation after 1196 hours exposure:

Sample #	4	Spectrum	#23
"	5	"	24
"	7	"	25
"	8	"	26
"	9	"	27
"	10	"	28
"	11	"	29
"	12	"	30
"	13	"	31

Sample showing no degradation after 2016 hours exposure:

Sample # 3   Spectrum #32

Samples showing any significant sign of degradation:

Sample #	0	Spectra	#33-36
"	1	"	37-39
"	2	"	40-41
"	6	"	42-44
"	14	"	45-48

SPECTRUM 23. Infrared Transmission Spectrum--Sample 4 (1196 hours)

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SPECTRUM 24. Infrared Transmission Spectrum--Sample 5 (1196 hours)

SPECTRUM 25. Infrared Transmission Spectrum--Sample 7 (1196 hours)

SPECTRUM 26. Infrared Transmission Spectrum--Sample 8 (1196 hours)

SPECTRUM 27. Infrared Transmission Spectrum--Sample 9 (1196 hours)

SPECTRUM 28. Infrared Transmission Spectrum--Sample 10 (1196 hours)

SPECTRUM 29. Infrared Transmission Spectrum--Sample 11 (1196 hours)

SPECTRUM 30. Infrared Transmission Spectrum--Sample 12 (1196 hours)

SPECTRUM 31. Infrared Transmission Spectrum--Sample 13 (1196' hours)

SPECTRUM 32. Infrared Transmission Spectrum--Sample 3 (1196 hours)

SPECTRUM 33. Infrared Transmission Spectrum--Sample 0 (93 hours)

SPECTRUM 34. Infrared Transmission Spectrum--Sample 0 (228 hours)

SPECTRUM 35. Infrared Transmission Spectrum--Sample 0 (383 hours)

SPECTRUM 36. Infrared Transmission Spectrum--Sample 0 (1196 hours)

SPECTRUM 37. Infrared Transmission Spectrum--Sample 1 (1089 hours)

SPECTRUM 38. Infrared Transimssion Spectrum--Sample 1 (1717 hours)

SPECTRUM 39. Infrared Transmission Spectrum--Sample 1 (2187 hours)

SPECTRUM 40. Infrared Transmission Spectrum--Sample 2 (1089 hours)

SPECTRUM 41. Infrared Transmission Spectrum--Sample 2 (1538 hours)

SPECTRUM 42. Infrared Transmission Spectrum--Sample 6 (93 hours)

SPECTRUM 43. Infrared Transmission Spectrum--Sample 6 (228 hours)

SPECTRUM 44. Infrared Transmission Spectrum--Sample 6 (547 hours)

SPECTRUM 45. Infrared Transmission Spectrum--Sample 14 (383 hours)

SPECTRUM 46. Infrared Transmission Spectrum--Sample 14 (547 hours)

100

SPECTRUM 47. Infrared Transmission Spectrum--Sample 14 (852 hours)

SPECTRUM 48. Infrared Transmission Spectrum--Sample 14 (1196 hours)

Discussion

In the samples that failed, similar degradation modes were evident (for comparison, original spectra #0, 1, 2, 6, & 14). We note that there are several consistent degradation signatures aside from the degradation of the 8-13 micron region. Considering the mechanisms discussed in section III.3.B., Polymer Degradation, we can reasonably identify these new spectral peaks. As the auto-oxidation chain reaction progresses, a variety of reaction products and intermediates are formed such as alkenes, alcohols, aldehydes, ketones, carboxylic acids, and more branching as well as more fissioning of the polymer backbone. Referring now to the spectra, we can locate evidence of a variety of these products as indicated below. One should keep in mind, however, that the degradation products vary with the type of stabilizer used as well as the conditions.

<u>Major Area of Peak Growth</u>	<u>Description of Potential Culprits</u>
2.5-3.1 μ (3640-3200 cm^{-1})	O--H alcoholic hydrogen stretch
3.3-4.0 μ (3000-2500 cm^{-1})	O--H carboxylic acid hydrogen stretch
5.6-6.0 μ (1780-1670 cm^{-1})	C=O carbonyl stretch
6.1-6.5 μ (1650-1550 cm^{-1})	C=C Carbon double bond stretch
8.0-10.0 μ (1250-1000 cm^{-1})	C--O Carbon oxygen bond stretch
10.0-13.5 μ (1000-750 cm^{-1})	C=C Carbon double bond out of plane bend

As for the individual samples, we see that the 6 mil control sample began to degrade immediately (first spectrum at 93 hours exposure) in most all of the above areas with significant degradation in the 8-13 micron area. The sample disintegrated after 950 hours but had been brittle (i.e. broke upon folding) for a considerable time before that. The first spectra taken for the 6.0 mil samples containing Methyl Zimate and Polygard as the synergists for ZnO were after 1089 hours (samples 1, & 2). Both of these samples showed significant spectral degradation at this time with the Polygard sample being brittle. The Methyl Zimate sample had not lost its structural integrity after over 2000

hours of exposure although the 8-13 micron degradation was significant after the first 1000 hours. Finally, the 6.0 mil ZnO sample with Ferro AM-105 as synergist has not shown any significant infrared spectral degradation although it has yellowed considerably. We believe this is due to the high level of synergist (1.0% by weight) compared with thinner sample 4 which has 0.5% and has not significantly yellowed. In addition, the yellowing is thought to be a result of impurities in the synergist (53).

Most of the thinner samples have shown little or no signs of degradation after 1196 hours of exposure. Sample 14 was expected to behave poorly as the antioxidant (Irganox 1010) did not compound well in the master batch. Sample 6 is an anomaly as this was one of our favorites, and still is. This sample is the 2.0 mil blown film version of the same formulation as the pressed sample 5. Sample 5 has shown no signs of degradation and so we conclude that somewhere in the preparation of #6 some form of impurity and/or greater heat history was introduced. This is under investigation. The most interesting part about the degradation of sample 6 is that it physically disintegrated before complete degradation of the spectral regions (after taking spectrum 44 the sample lost all integrity).

Using the previously defined concept of 'failure' we can assign an improvement factor to the samples tested.

<u>SAMPLE</u>	<u>IMPROVEMENT FACTOR</u>
0	1 (failed at 100 hours)
1	< 10 *
2	< 10 *
3	> 20 (spectral) **
6	2.5
14	10
all others	> 12 **

* Samples had 'failed' before infrared monitoring began.

** Samples have yet to fail in testing program.

III.4.D. Methodological Improvements

The only addition necessary in the optical testing area is to perform diffuse solar transmission on the clear glazing samples.

As for the weather testing, some improvements can be made in future experiments. First, only the three outboard bulbs will be sunlamps while the center bulb will be a heat lamp (if necessary) to sustain the appropriate temperature. This will prevent any uneven UV exposure of the center most portion of outboard samples. The original purpose of the center UV lamp was for super accelerated testing which we chose not to employ. Future super accelerated testing will be performed using a similar machine without the pyrex filters. Lamp changing will occur on a rotation basis where one of the three lamps will be changed each 330 hours. This will be done to even out the lamp intensity degradation over time (see figure 17). A water spray system may be employed to simulate rain and dew conditions but the value of such an addition is still uncertain.

FIGURE 17

SUNLAMP INTENSITY DEGRADATION W/TIME

IV. SUMMARY CONCLUSIONS AND FUTURE WORK

IV.1. Selective Emitter

Our research into selective emitter materials found silicon oxynitride to be an ideal material for reasons of optical selectivity, environmental durability, and cost of production. The following list includes some of the needed research to be pursued:

- 1) Locate source of SiO_xN_y powder, compound powder into polyethylene, make film samples using a variety of x and y values, and measure properties.
- 2) Produce SiO_xN_y film on aluminum foil via CVD and measure properties.
- 3) Using samples of SiO_2 and Si_3N_4 amorphous powders, compound mixtures into polyethylene and make film samples.

IV.2. Glazings

IV.2.A. Solar Transparent Glazing

Our research in this area demonstrated enhanced polymer lifetime possible through use of a variety of solar transparent additive combinations. Determination of the best formulation awaits completion of accelerated weather testing. Five of the six transparent formulations (three thicknesses), however, show no spectral or physical degradation after 1200 hours of accelerated testing or an improvement factor of greater than 12. Though direct comparison to outdoor weathering is difficult, an acceleration factor of 10 is considered conservative for our device.

Further work with non-polymeric additives will include experimentation with new additive combinations in an effort to find new synergistic formulations. The next few paragraphs will discuss the use of polymeric stabilizers for polymer lifetime enhancement.

A major problem with the use of non-polymeric UV absorbers is loss of absorber from the polymer due to exudation, volatilization, and solvent extraction. It should be noted that this is especially problematic in the case of thin-film low-density polyethylene (LDPE). One solution to this problem is to incorporate the absorber directly into the polymer by block or graft copolymerization (Bailey and Vogl, 1976) (54). Block copolymerization of absorber and polyethylene is not practical at this time, because it involves developing a new gas-phase polymerization from ethylene. Gas-phase polymerization has been optimized for high-volume production of polyethylene; and any attempt to adapt this process to specialized, low-volume production is not likely to be cost-effective. In addition, the block copolymerization of small amounts (less than 1%) of UV absorber into the aliphatic chain can adversely affect the mechanical properties of the polymer crystallinity, which is quite high in the case of polyethylene.

One approach to reducing absorber volatility is to produce a high molecular weight (m.w.) absorber. This approach is just recently being commercialized. National Starch has limited production quantities of Permasorb MA: a 2,4 dihydroxybenzophenone with a reactive vinyl group. Permasorb MA can be copolymerized with methyl methacrylate (MMA). The copolymerization process has been sent to us by Albert Micchelli of National Starch.

Cyasorb UV-2126 is a 2-hydroxy-4-acylethoxybenzophenone attached to a polyethylene chain, essentially the same as Cyasorb UV-531 attached to a polyethylene chain. Logically, it is the most appropriate choice for a polyethylene-compatible benzophenone. Its long aliphatic chain fits nicely into the crystal structure. American Cyanamid has no testing information or compatibility charts available on UV-2126, but Modern Plastics Encyclopedia (55) lists it as being compatible with polyethylene.

Ami Gupta suggests that this type of polymer-specific approach may be most appropriate to decreasing exudation. One problem to keep in mind is that adding long polymer chains to UV absorbers effectively dilutes the concentration of active

absorber units. Thus, the amount of additive that must be used for the same UV screening increases; and this approach ends up as a masterbatch, in which the additive is in high concentration (10-20%) copolymerized with ethylene. This masterbatch is mixed in a high (5-10%) concentration with bulk polyethylene to yield the final product. The masterbatch technique of compounding is commonly used in the plastics industry. However, it involves synthesizing increasing amounts of additive, which can be difficult in the case of gas-phase polymerization.

Another approach is graft copolymerization of UV absorber to the polymer chain. Ami Gupta has performed experiments along these lines for the Low-Cost Solar Array Project to lengthen the life time of ethyl vinyl acetate (EVA). The UV monomer used is a reactive benzotriazole, which becomes covalently bound to the EVA during cross-linking. While this approach is not directly applicable to polyethylene, Dr. Gupta says that he has a method for accomplishing cross-linking of reactive benzotriazole to polyethylene. Dr. Vogl's group at U. Mass., Amherst, has also synthesized reactive 2,4 dihydroxybenzophenones (56), methyl vinylsalicylates (57), and reviewed recent work in the area (58).

IV.2.B. Solar Reflective Glazing

Research in this area uncovered three potential pigments for use as 8-13 micron transparent solar reflective pigments: ZnO , ZnS , and ZnTiO_3 . Of these three, ZnO was chosen for its lifetime enhancement properties despite the fact that it had the lowest reflectivity. It was shown that nickel chelate additives perform better for both optical and lifetime enhancement properties than the other synergist used. One 6.0 mil sample has lasted over 2000 hours, improvement factor of over 20, with no 8-13 micron spectral degradation. Some yellowing of this sample has occurred but is thought to be due to impurities in the synergist. Two of the thin samples have lasted over 1200 hours, improvement factor of over 12, with no degradation.

Resultant reflectivity of 2.0 mil glazing was somewhat less

that 25% of the solar spectrum at air mass II. Though this is a rather disappointing figure, it must be realized that our main efforts were focused toward lifetime enhancement in this study. Below are listed several means by which we propose to dramatically increase the glazing's solar reflectivity and/or decrease transmission:

- 1) Higher loading of ZnO through use of titanates (surface treating chemicals).
- 2) Use of other more highly reflective pigments such as ZnS and ZnTiO₃ in conjunction with the ZnO (the ZnO should be used in any instance due to its life enhancement properties).
- 3) Using larger particle sized ZnO. It was determined that the ZnO currently utilized was engineered for high optical transmission. This would involve somewhere between a two to four time increase in particle size.
- 4) Prepare solar absorbing underlayer (also transparent to 8-13 micron radiation). This would involve the use of selectively absorbing (non infrared emitting) pigments compounded into polyethylene and coextruded with the reflective layer. Because black pigments are often very efficient and because the amount of light to be absorbed is small (most reflected by first layer), this layer need not be very thick in relation to the first.

IV.2.C. Resin

Lastly, there are two issues that can be addressed regarding the resin itself. Firstly, there is the large percentage of background radiation which is not directly related to specific structures. It would be most interesting to determine from where this background originates and if it can be eliminated. Secondly, it has been shown that linear polyethylene has a much lower tendency to auto-oxidize than branched polyethylene due to its high degree of crystallinity (59). Use of this material may significantly increase the lifetime of a glazing system. In addition, any method of film preparation which enhances crystallinity will enhance film lifetime.

V. APPENDICES

APPENDIX V.1

SENSITIVITY ANALYSIS CALCULATIONS

Calculation procedure:

1. Estimate ΔT , then determine a linear $W/m^2/^\circ C$ at $\Delta T/2$ from $E = AT^4$.

2. Write heat balance ledger at ambient $^\circ K$.

$$Q_{in} = Q_{sky} + Q_{glazing}$$

$$Q_{in} = Q_{sky \ 8-13} + Q_{sky \ not \ 8-13} + Q_{glaz \ 8-13} + Q_{glaz \ not \ 8-13}$$

3. .32 fraction energy 8-13
.68 fraction energy not 8-13

4. Get transmission by assuming that it is stated transmission plus one-half the absorbed portion times the emissivity of the emitting surface, i.e., iterate the exponentially decaying sum of interreflections once to get a good approximation of ΣT .

5. Treat glazing as a gray emitter whose emissivity is one-half its optical absorptivity.

$$Q_{in} \approx \left[Q_{sky} = (\epsilon_{surf. \ 8-13})(F_{8-13})(\tau_{glaz \ 8-13})(\epsilon_{sky \ 8-13})(AT^4) + (\epsilon_{not})(F_{not})(\tau_{glaz \ not})(\epsilon_{glaz \ not})(AT^4) \right]$$

contribution of sky $\uparrow$

$$+ \left[Q_{glaz} = (\epsilon_{surf. \ 8-13})(F_{8-13})(\epsilon_{glaz \ 8-13})(AT^4) + (\epsilon_{surf \ not})(F_{not})(\epsilon_{glaz \ not})(AT^4) \right]$$

$$Q_{out} \approx (\epsilon_{surf \ 8-13})(F_{8-13})(T_{glaz \ 8-13})(AT^4)$$

$$+ (\epsilon_{surf \ not})(F_{not})(T_{glaz \ not})(AT^4)$$

$$\sum_{All} Q_{flux} = Q_{out} - Q_{in}$$

then construct a linear equation:

then construct a linear equation:

$$Q_{\text{flux}} = -(\epsilon_{(\text{sky} + \text{glaz})})(Q_{\text{in}}/T) \Delta T \\ + Q_{\text{flux at } \Delta T = 0}$$

where:

Q = radiant heat flow W/m^2

surf = emissivity surface

"not" = "at wavelengths other than 8-13 microns"

"8-13" = "8-13 microns"

F = fraction of energy in that wavelength range

Q_{sky} - radiant heat from sky

Q_{glaz} - radiant heat from glazing

T_{glaz} - transmission of glazing corrected for multiple reflections.

Thus for selective surface,

$$T_{\text{glaz not}} = .8, T_{\text{glaz 8-13}} = .9, \epsilon_{8-13} = .9, \epsilon_{\text{not 8-13}} = .1$$

$$AT^4 = 460 \text{ W/m}^2, \epsilon_{\text{sky 8-13}} = .6, \epsilon_{\text{sky not 8-13}} = .9,$$

$$Q_{\text{convective}} = 1.0 \text{ W/m}^2$$

$$\begin{array}{rcl}
Q_{in} = Q_{sky} = & (.9)(.32)(.95)(.6)(460) & = 75.5 \text{ W/m}^2 \\
& (.1)(.68)(.90)(.9)(460) & = 25.3 \\
+ & & \\
Q_{glaz} = & (.05)(.32)(.9)(460) & = 6.6 \\
& (.1)(.68)(.1)(460) & = 3.12 \\
& & \hline
& & 110.05
\end{array}$$

$$\begin{array}{rcl}
Q_{out} = & (.90)(.1)(.68)(460) & = 28.15 \\
& (.95)(.9)(.32)(460) & 125.85 \\
& & \hline
& & 154.00
\end{array}$$

$$Q_{net} = 154 - 110.5 = 43.51$$

composite emissivity of sky-glazing-sol. Surf. :

$$\begin{array}{rcl}
(.9)(.32)(.95)(.6) & = & .16 \\
(.1)(.68)(.90)(.9) & = & .05 \\
(.05)(.32)(.9) & = & .01 \\
\hline
\epsilon & = & .22
\end{array}$$

$$Q_f \approx - (.22)(5.12) \Delta T + 1.0 \Delta T + 43.51$$

at stagnation, $Q_f = 0$,

$$2.12 \Delta T = 43.51$$

$$\Delta T \approx 20.5^\circ \text{C.}$$

This provides the second point for the linear plot.

V.2. Parties Recieving Glazing Samples

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