PNL-2824
UC-62

Weathering Characteristics of Potential Solar Reflector Materials: A Survey of the Literature

H. L. Hampton
M. A. Lind

September 1978

Prepared for the U.S. Department of Energy
under Contract EY-76-C-06-1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

Battelle

PNL-2824

Cat No: 23.0451

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy $____*; Microfiche $3.00

*Pages	NTIS Selling Price
001-025	$4.00
026-050	$4.50
051-075	$5.25
076-100	$6.00
101-125	$6.50
126-150	$7.25
151-175	$8.00
176-200	$9.00
201-225	$9.25
226-250	$9.50
251-275	$10.75
276-300	$11.00

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WEATHERING CHARACTERISTICS OF POTENTIAL SOLAR REFLECTOR MATERIALS: A SURVEY OF THE LITERATURE

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FOREWORD

This report is the result of a study performed for the Department of Energy Advanced Solar Thermal Power Systems Branch in support of the Materials Evaluation task of the PNL contract titled Solar Mirror Quality Assurance and Performance. Included in the task is a survey of the literature on the lifetime, durability and weatherability of potential solar reflector materials. The intent of the survey is to identify materials which could be useful in solar reflectors. The survey included optical properties, degradation mechanisms, accelerated and natural aging testing and performance evaluation techniques.

The initial phases of the survey used three computer data base services. The data bases searched under the DOE RECON system included Nuclear Science Abstracts (1967 to June 1976) and the Energy Data Base (1974 to present). The data bases searched via the Lockheed DIALOG System included the National Technical Information Service (1974 to present), Science Abstracts (1970 to present), Chemical Abstracts (1970 to present) and Engineering Index (1970 to present). Published searches compiled by the Smithsonian Science Information Exchange were also included. In addition, numerous limited distribution publications from private companies and various DOE laboratories were used. Some of the key words and phrases used for the initial search are included in appendix A for reference.

The initial phase of the search yielded over 9000 titles and abstracts. These were scanned to yield over 600 core articles containing pertinent information and references to begin a more comprehensive search.

This report gives a brief synopsis of the literature that was reviewed in detail. Despite the large amount of literature investigated, very little useful information was obtained in the degradation of the materials due to outdoor weathering. In particular, information on the optical properties of the materials is almost non-existent.

Due to the nature of this survey, the authors have stated the results and opinions found within others' work. No attempt has been made to verify any statements or conclusions found in these works and it is not within the scope of this survey to perform such verifications. The survey is intended solely to provide useful information and references on material weathering and testing and does not represent the opinions of the Pacific Northwest Laboratory or its sponsors.

CONTENTS

SUMMARY

A review of the available literature on the weatherability/durability of materials with possible applications in solar reflectors is summarized. A number of techniques used to weather solar materials are reviewed. These include both natural and simulated weathering. Little correlation has been shown to exist between natural and accelerated weathering, and much work needs to be done before results of accelerated aging tests can be used with confidence to predict material lifetimes under outdoor exposure conditions.

Some of the techniques used to measure or monitor material degradation are discussed. Emphasis in the literature has been placed chiefly on mechanical properties or appearance oriented measurements. The need is apparent for more detailed optical measurements of materials properties that are directly useful in engineering design. Although a great deal of literature is available on the materials described in the survey, there is very little solid data on the properties important for solar applications. A brief discussion of some of the applicable data on polymeric materials and glass is presented and referenced. The importance of cleaning solar materials is emphasized and some attempts at modeling degradation are discussed.

INTRODUCTION

The economic viability of solar energy conversion systems is dependent upon the service life of the materials used. The accurate prediction of the lifetime of these materials is necessary in order to perform a realistic cost/benefit analysis for working systems. Many of the materials including those used in solar reflectors are subject to the adverse and variable effects of terrestrial weathering. This report summarizes the results of an extensive literature survey which was undertaken to assess the present "state of knowledge" of the weathering characteristics of materials with optical properties that are suitable for solar reflector applications. The report emphasizes polymeric materials that could have immediate or near-term applications. Evaluation techniques, testing procedures and modeling are also discussed.

WEATHERING TECHNIQUES

A number of natural or simulated weathering techniques have been used to evaluate the performance and estimate the lifetime of solar materials. Natural weathering exposure is performed by commercial firms in several geographical locations. These include Desert Sunshine Exposure Testing, Phoenix, Arizona; Carribean Testing Inc., Caquas, Puerto Rico; Solar Testing Services Inc., Pampano Beach, Florida; South Florida Testing Service, Miami, Florida; Air Pollution Control Center, Cleveland, Ohio and others.[1] Natural weathering is commonly accomplished by exposing the samples on a fixed exposure rack which is tilted at an angle close to the latitude of the geographic location or on a rack which tracks the sun. Simulated weathering is standard practice for many materials producers. Commonly accepted methods of performing the simulations can be found in the standards and recommended practices of the ASTM, ASME, ASHRAE and other voluntary standards organizations.

It is generally recognized that there are many stress parameters which may effect the ultimate performance of a given material. The most commonly used stresses are temperature, moisture and UV radiation. The effects of ozone, sulfates and other atmospheric pollutants may also be important. In some cases even biological attack of the materials is significant. The effects of abrasion and mechanical stress can degrade the optical properties of some materials. The list may be extended indefinitely. These stress factors may degrade the material alone or they may act synergistically with other parameters to change the rate character of the degradation. This makes weathering an extremely complex phenomena.

Accelerated weathering tests are performed by either simulating the weathering stress factors believed to be most significant for the material being tested or by concentrating the natural weathering elements using higher, longer or more severe exposures. Examples of machines which concentrate natural environmental parameters are the follow-the-sun solar concentrators, EMMA (Equatorial Mount with Mirrors for Acceleration) and EMMAQUA (an EMMA with distilled water spray for 8 minutes out of each hour of operation).[2] These machines concentrate sunlight by a factor of 8 to 12 times that of the normal exposure. Devices used in simulated weathering tests include the Atlas 600 series Weather-Ometer, General Products All-Purpose Accelerometer (GPAPA), General Electric G30T8 Germicidal Lamp (CALBOX), and others.[3] These devices generally use a single or combination of xenon, carbon, or mercury arc lamps for light exposure. They may also be equipped to control and cycle various other weathering parameters (humidity, temperature, etc.).

Although these weathering machines are sometimes useful in ranking materials, much controversy exists concerning the validity of correlating the results obtained using such devices with the results obtained for natural outdoor exposure. For instance, Grossman states that natural wetness has a relatively long time cycle, 12-16 hours in length.[4] He emphasizes that the rate at which water permeates a polymer is time dependent and simulators should use water cycles on the order of 8-16 hours with a 40% wetness time. Rapid cycling of water and UV energy does not allow water enough time to carry out its oxidation function. He also states that aerated water should be used for spraying samples to simulate actual rainwater and temperature should be used as an accelerator. When compared with the operation of the EMMAQUA apparatus which uses 8-minute wetting times cycled every hour, distilled water for sample spraying, and intensified insolation for acceleration, it is of no surprise that differences exist which lead one to question the results of these tests. As another example Isakson has stated that the Atlas Dew Cycle Weather-Ometer is a severe degradation device and should not be used to represent acceleration of natural weathering because it produces large quantities of ozone and has excessive short wavelength energy.[21]

Despite these findings, good correlations relating some materials properties to natural weathering have been reported using accelerating machines.[1,5] In general the best correlations are usually obtained when a single stress parameter which is independent of other synergistic effects can be identified and used. Unfortunately, this is not usually possible for most materials.

A number of tests are used to measure or monitor materials degradation. Most of the emphasis in the literature is on the mechanical properties of the materials (tensile strength, elongation, hardness, creep, etc.), and very few references are made to the optical properties. When optical characteristics are reported, measurements are generally visual or appearance oriented. These include measurements of yellowing, fade, gloss, haze, warpage, color and clouding.[6,7,8,9,10] These measurements have found only limited usefulness and are of practically no value for the engineer designing a solar conversion system. Only recently have detailed optical measurements data of use to the design engineer appeared in the literature.

In the early literature, the most commonly reported optical parameter for solar materials is transmittance. However, this parameter is often reported in a manner that is of little value to the engineer. For example, transmittance is often quoted relative to a control material with unknown properties or integrated total transmittance is reported with no reference to the integration technique.

The more recent literature does include some information on measurement techniques, and the data is in a format which is more applicable to solar conversion systems. In these reports, spectral transmittance or reflectance data is obtained using spectrophotometric and integrating sphere techniques.[3,11,27] Useful measurements of specular reflectance are being made using bi-directional reflectometry, goniophotometry and other techniques.[5,12,13,14,15,16]

A number of optical methods have been used to monitor the degradation of solar reflector materials. One measurement that is commonly used to assess polymer aging is to monitor the material's transmittance at 360 nm.[17,18,19] A change in the UV transmittance can be caused by photochemical reactions within the material and may therefore be indicative of the degradation of the polymer. Attenuated Total Reflectance (ATR) has also been used to monitor the weathering of solar materials.[19,20] This method uses infrared reflectance to detect the formation of carbonyl groups on the plastic surface which are indicative of the polymer degradation. The technique is not useful for all materials however. One report states that ATR does not appear useful for monitoring the degradation of clear films in accelerated tests.[20] Infrared specular reflectance measurements have also been used to study the degradation of polymer films. Still other methods include measuring oxygen consumption,[22] observing the height of the goniophotometric peak[5] and evaluating average molecular weight, viscosity, and the formation of volatile products.[23]

POLYMERIC MATERIALS

There are many materials that have potential application as second surface mirror superstrates. According to one report, over 153 specific polymeric materials have been identified for use in solar cell encapsulation alone.[24] Many of these same materials could be used for second surface mirrors. For convenience the polymeric materials covered in this report have been grouped according to their chemical nature with specific materials discussed within each class.

ACRYLICS

Of all the polymers surveyed, acrylics seem to be the most durable. In tests performed by the Rohm and Haas Company, acrylic compounds based on methyl methacrylate and butyl acrylate monomers demonstrate the highest outdoor weatherability. The acrylics are available in both thermoplastic and thermoset forms. Unmodified, acrylics are transparent and stable against discoloration. They are also light weight and show good resistance to weathering, breakage and chemical attack.[25] However, they have a relatively large coefficient of thermal expansion ($6\text{-}10 \times 10^{-5}$ in/in/°C)[26], and have been reported to exhibit some buckling when exposed in the high humidity conditions of Puerto Rico.[1] They are also flammable and have a softening point of about 250°F. They may become somewhat brittle with age or in cold environments.

Commonly used acrylic sheets include Plexiglas made by the Rohm and Haas Company and Acry-Pane made by Sheffield Plastics, Inc. These sheets may be extremely clear with transmission values exceeding that of glass.

Samples of the Rohm and Haas Company "Plexiglas 55", a crosslinked acrylic, were mounted on January 19, 1956 in Albuquerque, New Mexico on a 45° south facing rack and removed 17 years and 8 months later. Comparison to a similar, currently manufactured material showed no noticeable change in empirical formula. A significant reduction in glass transition temperature indicating a decrease in chain length was observed, and a small increase in brittleness with a 51% decrease in flexural strength at rupture was noted. Using spectrophotometric methods and weighting to a 6000°K black body spectrum, the solar transmittance shows only a 10% decrease for the aged material with approximately 7% of the loss caused by surface roughening and only 3% due to changes in the bulk transparency.[27] Another report states that after 120 days exposure in a Weather-Ometer, Plexiglass DR and Plexiglass V-811 retained 89% and 86% respectively of their original transmittance.[35]

UV radiation is the primary cause of degradation of acrylics.[21] Photodegradation of polymethyl methacrylate (PMMA) results in a decrease in viscosity and average molecular weight; it also contributes to the formation of small amounts of volatile products. Degradation is believed to be a combination of thermal and random chain scissions.[23] Projected lifetimes for acrylics in solar applications are generally quoted as 20 years.[27,19]

HALOCARBONS

The most commonly referenced product in this class of materials is FEP Teflon (DuPont). This flourinated ethylene propylene material has a solar transmittance comparable to that of glass and exhibits very good UV stability. Manufacturers claim that 15 years exposure in Florida resulted in no change in the original 93% transmittance of a 10-mil sample.[28] Although the specifics are not reported, they also claim that the material remained crystal clear with no change in tensile strength.

Tests performed on aluminized and silvered Teflon exposed at a level of ten suns for 34 weeks produced no loss in transmittance.[29] In tests performed by Sheldahl, FEP showed no significant change in the 8 mrad specular reflectance after a 6-month exposure on an EMMAQUA apparatus.[13] In space, Teflon has survived 4600 hours of solar exposure with no detectable increase of solar absorbancy α_s.[30] In a NASA report, 1 mil samples of FEP lost only 5% solar transmittance after exposure to 16000 equivalent sun hours.[11] Other tests have shown that FEP has a high resistance to moisture.[12] Crosslinking resulting in embrittlement is the predominant aging mechanism.[24]

Teflon has two main disadvantages. It has unusually high processing temperatures which make it a relatively high cost ($6-$20/lb) material.[26] It also possesses a highly non-wettable surface which tends to attract and hold dust particles making it difficult to clean.

Another commonly referenced material in the halocarbon class is Aclar (Allied). This material does not exhibit the same high endurance properties of Teflon and becomes brittle under outdoor weathering conditions.[31] It also converts to a crystalline form at elevated temperatures (60°C).[32]

Poly vinylidene fluoride (PVF), another halocarbon, has excellent transmission characteristics and is relatively unaffected by solar radiation. One source states that after 10 years exposure in a semitropical ocean environment, PVF samples have not discolored and have retained 50% of their initial tensile strength.[24] Common names for PVF are Tedlar and Teslar (DuPont). Other common halocarbons are Teflon (TFE), PFA Teflon (E-TFE), and Viton (HFP-VDF) from DuPont; Kel F (CTFE), and Fluorel (HFP-VDF) from 3M; Halon (TFE), Plaskon (CTFE), and Halar from Allied; and Kynar (VDF) from Pennwalt.

SILICONES

Many silicone compounds have been identified for use in solar conversion systems. Many of these materials are not very specular but exhibit high values of normal hemispherical solar transmittance. They are generally quite stable to UV radiation but show a high water permeability resulting in dimensional changes of the material. The compounds most often identified in the literature are: RTV 602, RTV 655, RTV 566, RTV 615, RTV 560 (General Electric); XY-63-488, XR-63-489 (Dow Corning); Sylgard 182, Sylgard 184, DC-93500,[24] Silgrip SR-574[33] and DC-2103.[10]

The principle disadvantage of most silicones is their soft surface properties which allow particulates to become imbedded on their surface. One study rejected silicones for use as a solar cell encapsulent due to the permanently adhering accumulations of dirt after only 6 months of outdoor exposure.[34]

EPOXIES

Few references regarding epoxies were found in the literature although over 40 compounds have been identified for use in solar conversion systems. This is probably due to the fact that epoxies tend to darken when exposed to UV radiation and have been reported to lose 10-26% of the original transmittance in only 610 equivalent sun hours.[24] In outdoor exposure, epoxies show little change during the first 6 months but begin to darken after 1 year. At the end of 18 months, they exhibit severe chalking and considerable deepening of color. The epoxies are generally brittle and no satisfactory UV stabilizers exist for epoxy because of the absorbing nature of the resin.[10]

POLYESTERS

The most commonly referenced material in the polyester class is Mylar (DuPont). It is available in clear specular sheets and is quite flexible in this form (5 mil thickness). Mylar is available in a weather durable form suitable for solar use which is roughly 5% less transmissive than the regular form.

One test shows that the weather durable Mylar showed a 34% loss in transmission after exposure to mercury arc lamps for 5895 equivalent sun hours.[11] In a test performed by Sheldahl Inc., 5 mil weatherable mylar survived approximately 5 years outdoor exposure with saturated water vapor condensing on its back surface.[12] Other reports state that Mylar may become very brittle when exposed to outdoor weathering.[31] This has been found to be a characteristic of polyesters in general.[1] However, manufacturers claim that Llumar (Martin Processing Inc.), a UV protected polyester, has a useful life of 10 to 15 years or more in outdoor use.

POLYCARBONATES

The polycarbonates have received much attention in the current literature. The most commonly referenced polycarbonate is Lexan (General Electric). It is available in sheet form or it can be applied as a thin film for use as a protective coating.[35] Lexan is also available in a UV stabilized form for outdoor use although this form has been reported by some researchers as not suitable for solar applications.[36]

In one commonly reported degradation mode, a network of microcracks forms as a result of relatively short outdoor exposures (30-32 months). This cracking is due to a combination of light radiation and cycling of either temperature and moisture or temperature alone. The cycling is believed to induce stress fatigue and subsequent loss of strength. The cracks grow from the surface inward and are V shaped.[37]

Polycarbonates exhibit high impact resistance (4 to 6 times that of acrylic), high optical transmission (>80%) and are available in relatively specular forms (<2% haze). However, these materials exhibit poor solvent and abrasion resistance and show a high degree of yellowing. One report states that yellowing and clouding had occurred for Lexan samples after only 90 days of exposure.[18] Samples have also been reported to become brittle and retain only ∿25% of their tensile strength after 300 days exposure in Phoenix, Arizona or Miami, Florida.[17] The results of a number of test programs show that an acrylic face sheet bonded to a polycarbonate by means of an interlayer system is the most satisfactory method of protecting polycarbonates from degradation by outdoor exposure.[8]

POLYIMIDES

The material receiving the most attention in this class is Kapton, a DuPont Inc. product. Kapton has mechanical properties nearly identical to Mylar.[12] The film is flexible with outstanding radiation resistance but has poor initial optical transmission properties.[24] One test showed that Kapton buckles, tears, and breaks up in a relatively short period of time when exposed to outdoor weathering conditions.[1] The material was therefore rejected for use as a solar cell module cover material.

GLASS

Many non-polymeric materials are being considered for use in the construction of solar conversion systems. Glass is of particular interest in many of the concentrating systems. Several methods are referred to in the literature for the production of glass. The Foucault and Pittsburg process is performed by drawing the glass upward from a molten pool of glass. The Colburn or Libbey-Owens process draws the glass horizontally. In the Pilkington or float process, the glass is floated onto a molten pool of tin. In the Corning fusion process, the glass is allowed to overflow a trough-like container and fuse below the container. The gravity-drawn fusion glasses are comparable in flatness to the float glasses which fall into the 7 to 15 fringe per inch flatness range in thicknesses between .080 and .250 inches.[38] These glasses are of high enough quality to be specified for central receiver heliostat designs.[39]

The durability of glass to outdoor exposure is relatively good. Aging does occur by reaction of alkali ions in the glass with the water in air.[40] The rate of weathering may be largely determined by the rate of interdiffusion of sodium and hydrogen ions in the glass. Weathering becomes less prominent as alkaline earth ions are added to the glass. Periodic washing has been shown to prevent the buildup of weathering products and thus significantly reduce permanent damage.[41] Very few techniques are effective for monitoring the weathering of glass. Weight change, generated alkali, sorbed H_2O, electron microscopy and haze measurements have all been shown to be somewhat inadequate and the most commonly used technique is visual examination.[41]

OTHER CONSIDERATIONS

THE IMPORTANCE OF CLEANING

In general, cleaning affects the durability of many solar materials.

R. S. Berg has stated that the forces adhering particles to a surface increase fastest over the first 30-60 minutes of contact and level off after 24 hours at a level several orders of magnitude greater than the initial adhesion forces.[42] These accumulations have been shown to reduce the transmission of a horizontal glass plate by as much as 50% in only 14 days.[43] This problem is compounded for plastics which tend to attract particles more readily than glass and allow the particles to become imbedded in the soft surface making cleaning difficult and ineffective.

MODELING THE EFFECTS OF WEATHERING

Very few references were found that addressed the problem of modeling material degradation. Apparently, little work has been accomplished in this area. However, statistical modeling has been recognized as a necessary element in the expedient evaluation of systems lifetime under the effects of outdoor exposure.

In the limited number of references reviewed, several models were evaluated for use in the description of physical properties degradation in solar materials. These include simple exponential, normal or half normal, log normal, gamma, extreme value and Weibull.[45]

Much of the modeling to date addresses the wear-out mode of failure. This failure is caused by the gradual degradation of the properties which are directly related to the lifetime of the material.

The exponential model has been shown to be inaccurate when predicting the probability of a material failure within a time Δt during outdoor exposure. The model indicates that the failure rate is not a function of time. For instance, the model will predict that the chances of a material failure within the next 3 weeks will be the same for identical samples that have been exposed for 2 months and 24 months. In reality, the chances of the 24 month sample failing within the next 3 weeks are much higher than for the 2 month sample. The model does not agree with the physical situation it was meant to describe and should not be used.

The normal and log normal models are inadequate because they predict first an increasing then a decreasing failure rate. These models are given by the equation

$$Y = A \exp -[(x-u)^2/b^2]$$

where Y is the property being studied
x=t for the normal distribution
and x=log t for the log normal distribution

The gamma probability density function is undesirable as a first approximation principally due to its complexity. This model is given as

$$f(x) = \frac{\lambda^r}{T(r)} x^{r-1} e^{-\lambda x}$$

The Type 1 extreme value function (minimum) is given in the form

$$Y = \exp[-\exp(x)]$$

and meets the requirements of a decreasing function which asymptotically approaches the x axis. It also exhibits an increasing failure rate with time. The model may be adapted so that physical meaning may be assigned to the parameters. For instance, x may be replaced by (t-b)/a and b is related to the characteristic lifetime.

A Weibull function (one of the extreme value functions) was chosen in one study to model the loss in ultimate elongation as a function of time.[45] The Weibull model may be written as

$$Y = b_1 \exp\left[- \left(\frac{t+b_2}{b_3}\right)^{b_4}\right] + b_5$$

where Y is the percent retention of the property.

The following constraints and interpretations were found to apply to the parameters b_i:

b_1: >0, units of percent, is related to maximum property value ($b_1+b_5=$ max).

b_2: units of time, is related to pre-or-past-aging and in most cases is set equal to zero.

b_3: >0, units of time, is related to characteristic life (time to reach

37% of initial property value)

b_4: is related to shape of curve; $b_4 \leq 1$ indicates rapid initial decay; $b_4 > 1$ indicates induction period

b_5: $\geqslant 0$, units of percent, related to asymptotic value of the property

The model has been fitted to physical deterioration data for diverse types of plastics in different climatic areas. It was found to fit well, with 95% confidence intervals established for the calculated parameters.

The Weibull model has been used by others to model the loss in transmittance of polymeric materials as a function of the length of outdoor exposure with good results.[17]

Care must be taken to avoid prematurely accepting an incorrect model. Although small differences may exist between models over the near term data, extrapolations to long time intervals can yield varying predictions. For instance, one report fits a Weibull model, a log normal model and an empirical model to four data points obtained over 5 months of weathering. All models fit within the usual experimental errors; however, when the curves were extrapolated to yield characteristic lifetime the results ranged between 2.4 and 34 years.[17]

It is apparent from the results of this literature survey that there is insufficient accurate data in most cases for the proper evaluation of property modeling and the selection of the correct model. The need exists for further weathering studies of solar materials with an emphasis placed on obtaining accurate data on all of the weathering parameters (rain, humidity, insolation, etc.) as well as their effects on a periodic basis. Initial weathering studies need to be performed over longer periods of time so that models may be constructed iteratively. Models could then be used to extrapolate data obtained using accelerated weathering devices to accurately and rapidly predict the characteristic lifetimes of solar materials. This work will require controlled, highly instrumented experiments if meaningful results are to be obtained.

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APPENDIX A

KEY WORDS AND PHRASES
FOR LITERATURE SURVEY

APPENDIX A -- LITERATURE SURVEY KEY WORDS AND PHRASES

Coating
Coatings
Composite materials
Composites
Emissivity
Flat mirrors
Flat plate collectors
Glass
Glasses
Light Scattering
Mirrors
Optical dispersion
Optical properties
Optical reflection
Optical systems
Optics
Organic polymers
Parabolic reflectors
Photovoltaic cells
Plastics
Polymers
Protective coatings
Radiant heat transfer
Reflection
Reflectivity
Reflectors
Scattering
Silicon oxides
Silicon solar cells
Silicones
Solar cell arrays
Solar cells

Solar collectors
Solar concentrators
Solar energy
Solar energy conversion
Solar power plants
Solar radiation
Solar reflectors
Surface coating
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