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Some Chemical Aspects of Solar Energy Utilization*†

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For solar energy to have a significant impact on the energy economy of the United States, hundreds of square miles of solar collectors will have to be constructed. The chemistry of materials fabrication and stability will play an important role in the economics of collector fabrication and service life. This paper reviews some of the materials aspects of the materials involved and the environments to which they are exposed. In many cases, few data are available on the applicability of materials to solar applications.

Introduction

Solar energy may be utilized in a number of ways, both to generate and to conserve energy (*1*). These include (1) architectural design and construction; (2) low temperature conversion for hot water, space heating, absorption air conditioning, and agricultural uses; (3) high temperature conversion for electric power generation and industrial processing; (4) photovoltaic conversion to electric power; and (5) photoelectromechanical conversion to chemical energy (oxygen and hydrogen). The costs associated with solar energy utilization include (1) collection, (2) accumulation, (3) conversion, (4) storage, (5) conditioning for subsequent use, (6) maintenance, and (7) replacement. Any utilization scheme must make a systems analysis approach to determine both the feasibility and economics of each stage.

Figure 1 shows the solar spectrum and intensity external to the earth's atmosphere (AM0) and after passing through two standard atmospheres (AM2); also shown is the radiation spectrum of a blackbody at several temperatures. From the table, it can be seen that the solar radiation is primarily concentrated at wavelengths shorter than 2 μm while the blackbody radiation is at wavelengths greater than 2 μm. Thus, the first objective of solar energy collection for thermal applications is to convert the radiation in the band from 0.3 to 2 μm to a usable form and not to lose the energy by reradiation (*2, 3*).

Solar energy may be converted to thermal energy, electrical energy, or to chemical energy in the form of hydrogen and oxygen. A number of techniques and effects may be used to convert solar energy to a usable form (*1*) including thermal conversion, photovoltaics, photogalvanic, and indirect techniques such as wind, ocean thermal, and bioconversion. Solar conversion may use passive systems which utilize the absorbed energy locally such as in a greenhouse, or may be active systems which collect this energy as thermal (*4, 5*), electrical (*6–8*), or chemical (*9*), and transport it to another location. Depending on location and conditions, 10 to 50% of the total solar insolation will be diffuse and therefore will be unavailable for applications requiring focusing (*10*).

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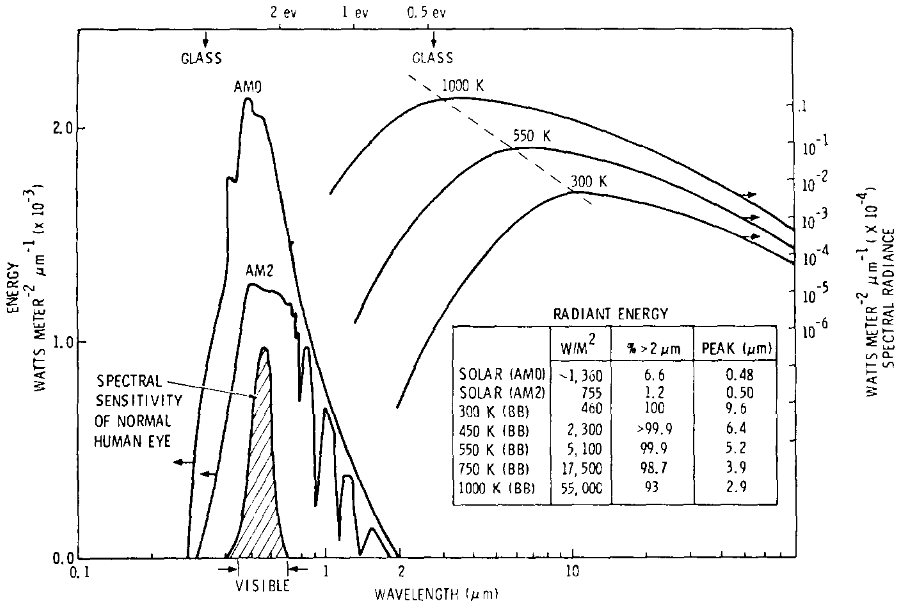

RADIANT ENERGY

	W/M^2	% >2 μm	PEAK (μm)
SOLAR (AM0)	~1,360	6.6	0.48
SOLAR (AM2)	755	1.2	0.50
300 K (BB)	460	100	9.6
450 K (BB)	2,300	>99.9	6.4
550 K (BB)	5,100	99.9	5.2
750 K (BB)	17,500	98.7	3.9
1000 K (BB)	55,000	93	2.9

FIGURE 1

Historically, electric power generation capacity in the United States has increased at a rate of 7.5% per year. Recently, this rate has decreased to about 4%, but this rate is expected to increase again as natural gas and oil become more expensive. The present (1975) United States electrical generating capacity is approximately 5 × 10^{11} W (*11*). A

TABLE I

	System							
		Solar thermal		Photovoltaic		Photo-		Ocean
Component	Passive	N-con	Con	N-con	Con	galvanic	Wind	thermal
Windows	*	*	*	*	*	*		
Mirrors	(*)[a]		*		*	(*)[a]		
Solar absorbers	*	*	*					
Thermal transfer (fluids/plumbing)		*	*		(*)[a]			*
Thermal storage	(*)[a]	*	*					
Electrical storage			(*)[a]	(*)[a]	(*)[a]	(*)[a]		
Insulation	*	*	*					
Sealants	*	*	*	*	*	*		*
Structural Components								
Air	*	*	*	*	*	*	*	
Ocean								*
Semiconductor components				*	*	*		
Chemical solutions (absorbers/ electrolytes)						*		

[a] (*) Possible use—N-con = nonconcentration, con = concentrating.

5% growth rate in generation capacity would be roughly equivalent to the construction of 50 new 500-MW electric power plants per year. If we take the AM2 solar insolation of 755 W per meter^2, assume 20% of this peak value as an average insolation value and assume ~10% solar-to-electric transmission conversion efficiency, a 500-MW (average) solar electric power plant will require 3×10^7 m^2 (~10 miles^2) of collector area. This means that to meet the projected 5% growth rate will require about 500 miles^2 of collectors to be built each year.

At the present time, a coal-fired electric power plant costs about $500/kW to install. Assuming 50% of the cost of a solar–electric power plant is in the collectors, an equivalent installation cost for the solar collectors would be about $5/m^2.

Space heating accounts for 18% of the energy consumption in the United States; of this, three-fifths is for residential heating. Solar heating is generally considered to be a supplemental heating source designed to handle 50–80% of the heating needs. There are about 6×10^7 dwelling units in the United States and this is expected to double by the year 2000 (*12*). If each of these new units were equipped with 1000 ft^2 of collectors, it would mean that 2000 miles^2 of collectors would be required.

TABLE II

MATERIALS

- Windows
  - Polymer
  - Glass
  - Reflecting
    - Solar
    - IR
  - Absorbing
    - Solar
    - IR
- Solar photothermal absorbers
  - Selective
    - Black chrome
    - Oxidized copper
    - Oxidized steel
  - Nonselective
    - Paint
- Thermal storage
  - Water
  - Rock
  - Salts
- Insulation
  - Fiberglass
  - Foams
  - Others
- Structural materials—Air
  - Metals
  - Polymers
- Semiconductor materials
  - Silicon—bulk
  - GaAs—bulk
  - CdS/Cu_2S—Thin films
  - SnO_x
- Mirrors
  - Reflectors
    - Metals
    - Metallized plastics
    - Metallized glass
  - Support
    - Polymers
    - Wood
    - Honeycomb
    - Metal
    - Concrete foam
- Thermal transfer fluids
- Boiler feedwater
  - High temperature/low vapor pressure fluids
  - Molten salts
- Electrical storage
  - Batteries
  - Pump liquid/turbine
  - Chemical
- Sealants
  - Silicone
  - Polysulfide
  - Others
- Structural materials—ocean
  - Metals
  - Polymers
- Encapsulants/protective coatings
  - Polymers
  - Inorganic

TABLE III

ENVIRONMENT

- Windows/mirrors
  - Rain/hail
  - Wind fatigue/loading
  - uv radiation
  - Thermal stress
  - Dust
  - Component outgassing
  - Cleaning
- Thermal transfer fluids
  - Impurity pickup
  - Metal/plastic
  - Thermal cycling
  - Flammability
  - Corrosion
  - Toxicity
- Sealants
  - Thermal cycling
  - uv radiation
  - Moisture
  - Hot/cold
  - Thermal expansion
- Semiconductor materials
  - Moisture
  - Pollutants
  - Thermal stress
- Solar photothermal absorbers
  - Air/vacuum
  - uv radiation
  - High temperature
  - Moisture
  - Thermal cycling
  - Component outgassing
  - Dust
  - Cleaning
- Structural cleaning
- Air/ocean
  - Salts
  - Pollutants
  - Wind loading
  - uv radiation
  - Moisture
  - Corrosion

For either solar–thermal or solar–electric to have a significant impact on the energy economy will require that hundreds of square miles of collectors be fabricated each year. To fabricate 1 mile^2 of material in 1 year requires a 3-ft-wide strip to pass by a given point at 20 ft/min continuously throughout the year. In addition, a square mile of 1000-Å film (density 5 g/cm^3) will require about 1 ton of material. Obviously, the key to solar energy utilization will be high volume–low cost production using low cost materials.

Chemistry may be important in the function of the energy conversion scheme, in the fabrication of the desired materials, or in the long-term performance of the components. A great deal of work has been done on the chemistry of energy conversion and storage; therefore, no attempt will be made to review these aspects of solar energy utilization. The high production volumes necessary will require development of chemical fabrication techniques such as electroplating, spray pyrolysis, gas phase polymerization. The principle purpose of this paper is to draw attention to the various materials and processes used in fabricating components for solar energy utilization. Generally there is very little information in the technical literature as to the suitability of the material in the environments encountered in solar energy utilization.

Table I lists the components of specific solar collection systems. Concentrating systems intensify the solar radiation by reflection or refraction prior to absorbing the radiation (*13*). Concentration ratios may be as high as 1000. Table II lists the more common materials used for the various components. Table III lists the environments to which the materials and components are exposed.

Components

Windows are used to retain heat in solar collectors by reducing convective and radiative losses and to protect the internal components of the collector from corrosion and contamination. Glass is an excellent window material though there are reflectance losses at each interface due to its rather high index of refraction (~1.5) (*14*). Impurities in the glass, primarily iron, can reduce the solar transmittance by absorption. Since glass is opaque in the infrared above about 4 μm it absorbs the thermal infrared. Antireflection coating and surface treatments can be used to decrease the reflectance losses, low iron glass can be used to increase transmittance, and solar-transparent infrared reflecting films of semiconductor materials (doped SnO_2 and In_2O_3) may be used to reflect the thermal infrared back into a collector.

Some polymers such as Tedlar^R are transparent in the solar spectrum and do not degrade on exposure to the ultraviolet radiation from the sun. These polymers are transparent to portions of the thermal infrared and do allow some radiation losses. Many polymers are not suitable as windows because they become brittle or disassociate on exposure to uv radiation. Some data exist for the outdoor aging of acrylics for 19 years (*15*). Spatial dispersion of the transmitted radiation is usually greater in polymers than in glass, particularly if the polymers have been treated to make them bondable. This spatial dispersion may increase with aging. This makes windows of these materials less suitable than glass where optical focusing of the transmitted radiation is desired.

Windows are exposed to the elements and rain, hail, and dust may affect them. Dust accumulation depends on the angle of repose and electrostatic effects. Polymers are particularly susceptible to dust accumulation because of the electrostatic charge built up by wind-borne dust. Cleaning the dust from the soft polymer surface can result in scratches which increase the spatial dispersion of the transmitted radiation. Hail may break the brittle glass if it is not strengthened. Wind fatigue may embrittle polymer windows causing them to fail (*16*). From a design standpoint, wind loading is a very important factor in window design. An often neglected degradation mode of windows is the condensation on the windows of moistures and vapors which have outgassed from other components. These condensed species can collect dust or absorb the solar radiation.

For some window applications, it is desirable to reject some of the incident solar radiation. This may be accomplished by using partially reflecting metal films on the window directly (architectural glass) or by applying the metal films to a plastic film which is bonded to the window. These films tend to corrode due to ineffective environmental protection. Another approach is to use a selective absorbing fluid in the window (*3*). A dilute solution of copper sulfate will absorb the infrared portion of the solar spectrum (~60%), but transmit most of the solar spectrum of which the eye is sensitive (~40%). This fluid can be circulated to keep the window cool and allow the thermal energy to be used elsewhere. Other fluids may be less expensive and have more desirable optical properties.

Mirrors are used to reflect the radiation to a desired location. In applications where the reflected radiation is to be focused, there must be little spatial dispersion on reflection. Reflectors are normally polished metals or metallized plastics or glass, though a white paint is a rather good diffuse reflector. Corrosion of the metal film or surface destroys the desired optical properties. Silver would be the best metal to use as a reflector, but the poor corrosion properties of silver precludes its use. Aluminum is the metal most often used. Since the mirror surface is often exposed to the elements, the reflecting surface is usually covered with a thin protective coating or film of polymer or glass. The reflecting surface is exposed to dust and corrosion which will decrease the reflectance, and cleaning will usually decrease the specular reflectance. Hail can be a disaster.

The reflecting surface of a mirror may be supported by a structure made of polymer, wood, foam, etc., which must be stable in order to retain the desired optical properties of the mirror. The same is true of any material used to bond the reflecting surface to the structure. Moisture may affect the supporting mirror structure.

Solar photothermal absorbers absorb the incident solar radiation and allow the thermal energy to be extracted (*17*). Usually the absorbers are coatings on a structural component. It is usually desirable that the absorbers have a high solar absorptance (α_s) and low thermal emittance (ε_{tH}). For most applications, a high α_s is desired even at the expense of an increase in ε_{tH}. The most generally used coatings are electroplated black nickel (nickel–zinc sulfides), electroplated black chrome (chromium oxide) (*18*), and copper oxides prepared by chemical conversion processes. Typically a thin coating (~2000 Å) of the solar absorber is formed on a surface which has a low infrared emittance, such as electroplated nickel. The coating absorbs in the solar spectrum; but because of its optical properties, it becomes transparent in the infrared and thus has a low infrared emittance. Paints usually have a high thermal emittance since the binders used have strong absorptance (high emittance) bands in the thermal infrared. A paint binder with low emittance in the thermal infrared would be highly desirable (*19*). All of the materials used for solar coatings have an appreciable volume emittance which means that the ε_{tH} is directly proportional to the coating thickness (*18*).

The semiconductor materials used for the selective coatings are often sensitive to the environment. Lead sulfide is a good selective coating material, but a combination of ultraviolet radiation and oxygen will convert the lead sulfide to lead sulfate, which is not a selective absorber material (*19*). The electroplated nickel–zinc sulfide is sensitive to moisture and temperature and is not stable in some applications. Multilayer coatings are often not stable with temperature due to interdiffusion. Absorber surfaces are often subjected to condensation of moisture and vapors from outgassing components. Dust accumulation may also be a problem on poorly sealed systems.

Sealants are used around the optical components of the collectors (windows and absorbers) and are often the source of long-term degradation. The seals are exposed to extremes of temperature, ultraviolet solar radiation, stressing by thermal expansion, and moisture. Failure of the seals allows moisture and dust into the collector and increases thermal losses. A good sealant must remain flexible at all temperatures and with aging. Design of the collector will often determine the long-term sealant performance. Polysulfide sealants are generally better than silicone sealants because of their greater flexibility at low temperatures.

Thermal transfer fluids are used to transfer heat from the collector to the storage/conversion system. Air, water, oils, and molten salts are most often used. Air has a poor heat capacity, but has the advantage that it is cheap and does not freeze. Water has a high heat capacity, but the system must be designed so that it will drain when the temperature is low or it must have additives which lower its freezing point. These additives are rather expensive and either large amounts are required or elaborate heat exchangers must be used. When using a water system, care must be taken to prevent corrosion. This usually requires additives and control of the chemistry of the system. For high temperature applications, water requires a pressure system because of its high vapor pressure.

Oils are interesting as thermal transfer fluids, and high temperature/low vapor pressure materials such as Therminol^R, are being used even though they are very expensive. Oils often present acceptance and building code problems because of their potential flammability. At high temperature, molten salts may be used as thermal transfer material (*20*) though there are probably corrosion problems with these materials.

Thermal storage may be simple or elaborate (*21*). Simple systems store sensible heat using rocks or water as a storage medium. Rocks are cheap and easy to handle, but only have one-fifth of the heat capacity of water. Water has a high heat capacity and by using stratification, thermal gradients may be generated in the storage system to allow various temperatures to be extracted. More complex storage systems may use eutectic salts where the heat associated with a phase change (latent heat) may give very high thermal storage capacities. Usually the eutectic salts require a nucleating agent and careful storage since corrosion and heat exchange are a problem. The use of reversible chemical reactions to store heat has not been investigated very extensively.

Insulation is important in the efficient use of solar–thermal energy. Insulation is used in the collector, all associated plumbing, and around the thermal storage system. Cost is a limiting factor in insulation utilization. A problem with any insulation exposed to the environment is degradation by moisture pickup. Some types of insulation are sensitive to degradation by ultraviolet radiation. Outgassing products from insulation may condense on windows, mirrors, or receiver changing their optical properties.

Structural materials are an important aspect of the solar collector system. Hundreds of square miles of collectors will be needed for solar energy to make a meaningful impact on the energy economy. Structural materials will be subjected to corrosion, mechanical fatigue, moisture, and ultraviolet radiation, and must not degrade under these conditions (*22*).

Copper, steel, and aluminium are the prime contenders for solar–thermal receiver materials (*23*).

Encapsulation will be required for semiconductor devices to avoid corrosion of the metallization and moisture condensation. The encapsulant materials and sealants will have to be stable in the outdoor environment, and the window portion will have to retain good solar transparency.

Protective coatings are desirable for fragile surfaces exposed to the outdoor environment or handling. Mirror surfaces, in particular, require a protective coating which may be a thin polymer sheet or a polymer film.

Fabrication

Table IV gives some of the techniques which may be used to fabricate components of the solar collector system which are normally thin films or coatings. Some of these techniques such as vacuum deposition on plastic sheet and windows and electrodeposition on strip steel, are well-developed, high volume techniques; while others such as chemical conversion coatings are low volume batch processes.

TABLE IV

FABRICATION TECHNIQUES—THIN FILMS AND COATINGS

- Reflectors
  - Vacuum processes
  - Spray pyrolysis
  - Electroplating
- Selective solar absorbers
  - Electrodeposition
  - Vacuum processes
  - Chemical conversion
  - Paints
- Polymer films
  - Solution
  - Gas phase polymerization
- Antireflection surfaces
  - Vacuum processes
  - Chemical etching
  - Chemical leaching
- Semiconductor films
  - Vacuum processes
  - Chemical vapor deposition
  - Spray pyrolysis
  - Chemical conversion

Some, such as spray pyrolysis of semiconductors, are relatively undeveloped.

In the electrodeposition of 10,000 Å of tin on strip steel, plants exist which have a capacity of 1.9×10^6 ft^2 per 8-hr shift or about 70 miles^2 per year (*24*). These plating lines coat strip steel moving at a speed of 1650 ft/min. There are about 700 miles^2 of strip steel tinplated in the United States per year. This technology might be applicable to the electro-deposition of selective solar-absorbing coatings or the metallization of flexible materials.

In the vacuum coating industry, there exist air-to-air strip coaters capable of coating a 5-ft-wide plastic sheet with 500 Å of aluminum at a rate of 600 ft/min with a throughput of about 5×10^8 ft^2 per year (*25*). A batch-type roll coater has a smaller throughput, but has a lower capitalization cost. Flexible substrates can be coated at a higher rate than can rigid substrates.

To coat individual rigid pieces requires an operation which is more labor intensive than the continuous-coating systems. One glass company has a continuous lock-type batch coater for depositing a two- or three-layer film on 10 × 12-ft glass panels (*26*, *27*). This system is reported to have a throughput of about 3×10^6 ft^2/year and uses electron beam evaporation sources. Sputter deposition systems for coating glass panels have been constructed (*28*).

Float-glass plants produce glass by pouring molten glass on a bed of molten tin, then allowing the glass to cool as a continuous sheet. Production rates from one such plant are 10 miles^2 of glass sheet per year (*29*). Conceptually, such a plant could be expanded to allow the spray pyrolysis deposition of metallic reflector surfaces, semiconductor infrared reflector surfaces, or CdS/Cu_2S solar cells at a rather low areal cost.

Fabrication costs are difficult to obtain (*30*, *31*). Tin plating of steel is done for several cents a square foot because of the high volume. A similar batch-type electroplating would cost \$1/ft^2. Multilayer, interference coatings on glass may cost as little as \$1.00/foot^2, but chemical leaching may cost much less. Plastics may be metallized at a cost of about \$0.01/foot^2 at high volume. If the fabrication of solar material can be combined with an existing production facility, the cost may be appreciably lower than if solar material is processed in a separate operation. This would be the case in spray pyrolysis on glass in a float glass plant (*32*). It should be recognized that the optical materials used will be determined by the economics, which in turn will be determined by the production technology and marketing costs. Many attractive materials/systems will fail in the economic analysis.

Summary

It is obvious that the chemistry of corrosion, aging, and environmental protection plays an important role in the fabrication, use, and stability of materials for use in solar applications. Protection of surfaces from the environment presents one of the greatest challenges since long-term stability will be a necessary property in order to achieve the economic goals. A very costly collector system may fail because of a poor sealant, so even seemingly trivial components will play an important part in developing a low cost, stable component. To have a significant impact, technology must develop low cost–high volume processes and materials designed to meet the specific requirements of solar energy utilization.

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