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Failure and Degradation Modes in Selected Solar Materials: A Review

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C. M. Lampert, Editor

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Failure and Degradation Modes in Selected Solar Materials: A Review

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Solar Heating and Cooling Program
Task 10: Solar Materials R&D

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Preface

INTRODUCTION TO THE INTERNATIONAL ENERGY AGENCY AND THE IEA SOLAR HEATING AND COOLING PROGRAMME

The International Energy Agency was formed in November 1974 to establish cooperation among a number of industrialized countries in the vital area of energy policy. It is an autonomous body within the framework of the Organization for Economic Cooperation and Development (OECD). Twenty-one countries are presently members, with the Commission of the European Communities (CEC) also participating in the work of the IEA under a special arrangement.

Collaboration among member countries in the research and development of alternative energy resources in order to reduce excessive dependence on oil is an important element of the IEA program. A number of new and improved technologies which have the potential for making significant contributions to global energy needs were identified for collaborative efforts. The IEA Committee on Energy Research and Development (CRD), supported by a small Secretariat staff, is the focus of IEA R&D activities. Four Working Parties (in Conservation, Fossil Fuels, Renewable Energy, and Fusion) are charged with identifying new areas for cooperation and advising the CRD on policy matters in their respective technology areas.

Solar Heating and Cooling was one of the technologies selected for joint R&D activities. During 1976-77, specific projects were identified in key areas of this field and a formal Implementing Agreement drawn up. The Agreement covers the obligations and rights of the Participants and outlines the scope of each project or "task" in annexes to the document. There are now eighteen signatories to the Agreement:

Australia
Austria
Belgium
Canada
Commission of the European Communities
Federal Republic of Germany
Denmark
Finland
Italy
Netherlands
New Zealand
Norway
Japan
Spain
Sweden
Switzerland
United Kingdom
United States

The overall program is managed by an Executive Committee, while the management of the individual tasks is the responsibility of Operating Agents. The tasks of the IEA Solar Heating and Cooling Program, their respective Operating Agents, and current status (ongoing or completed) are as follows:

Task 1	Investigation of the Performance of Solar Heating and Cooling Systems - Technical University of Denmark (Completed).
Task 2	Coordination of Research and Development of Solar Heating and Cooling - Solar Research Laboratory - GIRN, Japan (Completed).
Task 3	Performance Testing of Solar Collectors - University College, Cardiff, U.K. (Completed).
Task 4	Development of an Isolation Handbook and Instrument Package - U.S. Department of Energy (Completed).
Task 5	Use of Existing Meterological Information for Solar Energy Application - Swedish Meterological and Hydrological Institute (Completed).
Task 6	Performance of Solar Heating, Cooling, and Hot Water Systems using Evacuated Collectors - U.S. Department of Energy (Completed).
Task 7	Central Solar Heating Plants with Seasonal Storage - Swedish Council for Building Research (Ongoing).
Task 8	Passive and Hybrid Solar Low Energy Buildings - U.S. Department of Energy (Ongoing).
Task 9	Solar Radiation and Pyranometry Studies - KFA-Julich, Federal Republic of Germany (Ongoing).
Task 10	Solar Materials R&D - AIST, Ministry of International Trade and Industry, Japan (Ongoing).
Task 11	Passive and Hybrid Solar Commercial Buildings - Swiss Federal Office of Energy (Ongoing).
Task 12	Solar Building Energy Analysis and Design Tools - U.S. Department of Energy (Ongoing).
Task 13	Advanced Solar Low Energy Buildings - Norwegian Institute of Technology (Ongoing).

TASK 10 - SOLAR MATERIALS R&D

Task 10, Solar Materials R&D, was initiated to address the materials problems associated with improvements in cost, performance and reliability of solar hot water, heating and cooling systems. Task 10 activities began in 1985 and will be complete in 1990. The participants are presently focussing their efforts in the following areas:

Subtask A: Performance Criteria for New Solar Materials. Investigates systems and subsystem performance of new materials or proposed materials for solar use.

Subtask B: Selective Absorber Materials Involves the round-robin testing of absorbers for optical properties. Addresses issues of failure, degradation and effects of controlled stresses on the absorber properties.

Subtask C: Collector and Window Glazing. Covers the study of electrochromic optical switching devices, and testing and analysis of low emittance coatings and transparent insulation.

Subtask D: Heat Transfer and Thermal Storage Media. Involves the study of the stability of latent heat storage media and water-propylene gycol solutions.

The Task 10 participants represent the following countries:

Austria
Canada
Denmark
Federal Republic of Germany
Italy
Japan (Operating Agent)
The Netherlands
Spain
Sweden
Switzerland
United Kingdom
United States

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1. INTRODUCTION

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1. Scope of Study

It is widely known that most materials used in solar energy conversion and building energy control applications suffer from two major restrictions, the first being the cost effectiveness of the material in a particular use and the second being durability. In the solar field, cost has been a very important factor and has restricted development of more expensive but efficient materials. The issue of durable lifetime is coupled to the cost; since in many cases a more expensive material might have greater durability or operational lifetime. This investigation looks into selected solar materials and how they degrade, fail or cease to function in their specific solar application, and explores methods by which certain materials can have their operational life extended. This report documents work conducted as part of Task 10: Solar Materials R&D of the IEA Solar Heating and Cooling Program.

This study correlates known failure and degradation modes to applied stress or load conditions for selected solar materials. The specific materials were selected by the members of this international program. Researchers from six of the participating countries in Task 10 were involved in this study. For this study the authors are from England, Federal Republic of Germany, Japan, The Netherlands, Switzerland and the United States. The authors are acknowledged at the beginning of each respective chapter. The solar materials studied are drawn from the following four categories:

- Collector and Window Glazings
  (including low-emittance and optical switching materials)
- Collector and Absorber Materials
- Heat Transfer Media and Additives
- Thermal Storage Media (Latent Heat)

The determination of specific materials in each category to be covered was made by the authors in accordance with their interests and time constraints. The major materials of interest selected were:

A. Glass and Polymer Materials for Glazings

  1. Insulating glass units and low iron glass
  2. Sealants for glazings
  3. Polyethylene Terephthalate (polyester) polycarbonate, polymethyle methacrylate (acrylic) fiber reinforced plastics, and polyvinyl fluoride
  4. Optical switching materials
  5. Heat mirrors

B. Solar Selective Absorbers

  1. Cermets (Black Chrome)
  2. Anodized nickel pigmented aluminum
  3. Black zinc, Black Cobalt, Blue Stainless Steel
  4. Selective paints

C. Heat Transfer Media

  1. Ethylene glycol - water - inhibitor mixture.
  2. Propylene glycol - water mixtures

D. Thermal Storage

  1. Salt Hydrates, Pentaerythritol
  2. Polyethylene and Paraffins

Many of the above topics are covered in this study. There are many important materials missing from this list, notably reflector materials, holographic films used for concentrators, spectral splitting coatings and transparent insulation media such as aerogel. Some of these materials are new, so little stability and degradation data is known, but because of their importance they may be studied in a future IEA Task 10 activity.

2. Environmental Factors that Lead to Degradation and Failure of Solar Materials

Materials fail or degrade under the influence of applied stress which many times comes from the environment. The major stresses are detailed as follows:

A. Ultraviolet radiation

Many solar materials are influenced by UV radiation (290-400 nm). This radiation has sufficient energy to break some of the weaker chemical bonds in polymers. This stress is very significant to non-glass glazing materials. In addition, through UV radiation interactions, excited states and ionization can take place which can lead to unwanted chemical reactions.

B. Temperature

Thermal energy influences many degradation processes. The role of temperature can be a contributing factor in the kinetics of reactions and diffusion dependence. Many reactions are favored to form thermodynamically but are prevented kinetically from occurring.

C. Humidity and Moisture

Water in the form of liquid or vapor can cause corrosion and accelerate oxidation of metallic materials. This effect is significant in metal/dielectric/metal multilayer coatings and metallic surfaces or metal/oxide composite. Water can induce degradation of sealant materials by leading, hydrolysis, swelling and dissolution. Many polymers are degraded by the combination of high humidity and temperature.

D. Pollutants

Pollutants such as NO_x, O_3, SO_2, and particulates can degrade many solar materials. Generally, pollutants attack materials in a synergistic fashion as they combine with heat, water, and light. Long-term effects are usually seen and follow very complicated mechanisms. Pollutants can attack optical films exposed both indoors and outdoors. This is of particular concern to Dielectric/Metal/Dielectric type low-emittance coatings. Silver films are particularly sensitive to free sulfur which is in higher concentrations in the interior of office buildings.

E. Oxygen

Oxygen coupled with the UV radiation and elevated temperature can cause degradation of many polymers. Antioxidations are used to slow down this process. A common failure mode is oxidation for metals, semiconductors and composites, especially when temperature and moisture are involved.

F. Physical Stress

Both mechanical and thermally-induced stress can cause failure of glazings, sealants and collector substrates. Bonding failures at interfaces are common. Flaws generated by other degradation mechanisms can cause failure under normal physical stresses. Temperature cycles and wind forces can result in fatigue failure.

G. Abrasives, Dirt and Sand

Physical abrasion can contribute to the alteration of optical properties and cause surface flaws to form. Cementation of particles can lead to surface chemical reactions with moisture.

The data for the selected materials is reported using a matrix format presentation which allows for easy comparison of several studies using simple tables. Two matrix tables are used. The first is the Materials-Load Matrix. This matrix compares several materials within one of the four materials categories with the loading or stressing condition of the material. The results of such a matrix indicate the predominate loading conditions for a group of materials, e.g., glazings. The second matrix is the Degradation Modes - Load Matrix. This matrix indicates the predominate failure modes under similar and different conditions for specific materials. It also indicates the extent of research on the material and test conditions used.

- Matrix Reporting Format

Selected research studies describing a solar material and how it fails or degrades under an applied load are summarized on a Reference Reporting Sheet. The net results of several studies are presented in two matrix formats. Each material and applied load is indicated by an identification code (ID-code), for example, B7 = Blackchrome on nickel tested in humidity. This ID-code correlates the Reference Reporting Sheets to the Materials/Load Matrix. Also, on each Reference Reporting Sheet, for each material type, a number is assigned, which is used to correlate the Reference Reporting Sheet to the Failure and Degradation Mode/Load matrix. These are important since they detail where, when and the nature of each specific study.

- Material - Load Matrix

This matrix (see Fig. A) shows the relationship between several materials of the type under a range of loads. The number of references with the same ID-code is recorded in each matrix element. As a result, the main study topics will be indicated, along with any gaps or low numbers indicating where work is needed.

- Failure - Degradation Mode/Load Matrix

This matrix (see Fig. B) shows the mode of degradation caused by an applied load for each specific material or combination, as well as the detected failure of the coating. This

Material/Load Matrix

Number: Date:

Total number of considered reference reporting sheets:

Number of reviewed publications:

Load												
Material	1	2	3	4	5	6	7	8	9	10	11	12
A												
B												
C												
D												
E												
F												
G												
H												
I												
J												
K												

Figure A

Degradation Mode/Load Matrix

Number: Date:

Total number of considered reference reporting sheets:

Number of reviewed publications:

Load												
Material mode	1	2	3	4	5	6	7	8	9	10	11	12
A												
B												
C												
D												
E												
F												
G												
H												
I												
J												
K												

Figure B

matrix is an expansion of each materials line in the Material/Load Matrix. The number assigned each Reference Reporting Sheet for each materials type are used in this matrix. A complex ID-code might be B3-2, where the 2 signifies the second reporting study dealing with B3. By using this matrix a direct comparison between different studies using the same applied load, as well as the comparison of degradation modes caused by different loads, is possible.

2. COLLECTOR AND WINDOW GLAZINGS

Complete glazings for solar collectors and architectural windows are composed of a transparent material which is sealed into a frame. There are various versions of this basic design involving multiple glazings, fill gasses and functional coatings. The most popular choice for both collector and window glazings is soda-lime glass. Glass is probably one of the most inert materials in the world. The use of glass is followed by various plastic materials. The types of plastics that are generally used are acrylic, polycarbonate, polyvinyl fluoride, and polyester. These glasses and plastics have very good optical properties and their fairly small reflectance and absorption losses can be reduced by surface treatments and reduction of absorbing species in the material. The major drawback to glass is its poor impact resistance and weight. The drawbacks to plastics are long term stability (especially to UV light and oxidation) and softness. Plastics have some advantages over glass, as films they can be stretched and formed into various shapes, they are lightweight and safe to handle. Thin glass sheets have been used to form parabolic reflectors and have been proposed as inner glazing for windows.

There is considerable effort by the plastics manufacturers to make harder and more stable plastics. A combination of glass and plastic materials is fiber glass and is used in nonview glazings. One development in plastics is the creation of a protective fluorocarbon surface layer on an inexpensive plastic. Another area of research is the stabilization of plastics by using directly bonded stabilizers, antioxidants and plasticizers. This will make the additives actually part of the polymer chain; currently they are just additives.

A problem that plagues both glass and plastics is dusting and cementation of particles on the glazing surface. This results in considerable transmittance loss and system efficiency decline. Scheduled washing has been prescribed as the best solution to this problem. This problem has been the worst in arid or desert environments, where often water is very valuable and not available for washing. Certain fluorocarbon treatments are used to reduce dustings on architectural glazing, but such treatments require renewal every few years. The development of a glazing surface that would be resistant to dusting and particle cementation would be very useful to the glazing field.

The stability of glazing sealants is another important issue. No single sealant is known that is ideal for collectors on window glazing. Many sealants are permeable by water or gases. Also, many sealants outgas organic by-products. The few that have low permeabilities have poor mechanical properties. The best seals are made from dual sealants which work together to supply combined properties. For architectural gas fill or even advanced evacuated systems, seals become very important and they may be the weakest part of the system. The following subchapters cover aging modes of glass, polyester, sealants and electrochromic optical switching films for glazings.

Aging Modes of Glass in Windows and Solar Systems

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1. Introduction

Today, float glass is used in most windows. Float glass is a soda-lime silicate glass that is made by the float process, which consists of floating a continuous ribbon of glass on a bath of molten tin. This process leads to a glass with a smooth surface without polishing. Apart from the use of float glass in architectural windows, it is an important candidate as cover glazing for flat-plate solar collectors [1]-[4], as a protective window for photovoltaic cells [12] and as a superstrate for solar mirrors [8] and [11].

In view of these solar applications, float glass can be improved in various ways: The solar transmittance can be improved from about 82% to 90% for 4mm thick glass by reduction of the iron content (low-iron glass) or by control of the iron oxidation state. Antireflection layers can increase the solar transmittance even further, to an upper limit of about 96%.

The glass strength can be increased up to a factor of about 10 by tempering methods, including thermal or chemical treatments. Furthermore, there are glass formulations which are chemically more durable than float glass, such as borosilicate and aluminosilicate glasses. However, mostly soda-lime silica glass is preferred for solar applications due to economic reasons. The object of this paper is to briefly review and evaluate the possible aging mechanisms of float glass for application in architectural windows and glazings for solar energy conversion systems.

2. Failure and Degradation Modes

Glass generally has excellent properties for a glazing. Its greatest shortcoming is its poor resistance to physical impact. When glass is exposed to atmospheric conditions, it undergoes some physical and chemical changes. The optical properties (transmittance) can change by weathering and solarization and the strength of glass can decrease by stress corrosion. Abrasion of the surface of glass by blowing sand and dust will also decrease its strength. Also in many cases glass glazings fail by breaking either due to poor engineering design of the glazing frame for thermal expansion or by physical force. In Tables I and II are listings of degradation modes noted for low-iron glass subjected to various environments.

2.1. Weathering

Weathering of glass, or glass corrosion, occurs by reaction of the glass surface with atmospheric water in both liquid (by condensation, precipitation) and vapor form. Theoretical treatments of the chemical durability of glass and aqueous corrosion can be found in references [6], [7] and [9]. Two stages of corrosion have been distinguished: alkali leaching and network dissolution. In the first stage molecular [9] water penetrates into the glass and alkali ions are replaced by hydrogen ions. Outward diffusion of alkali ions leads to a dealkalized surface layer. Alkali leaching of the glass surface will always take place when glass is exposed to the atmosphere, but normally does not have severe optical consequences. The dealkalized surface film has a protective function against proceeding corrosion and will even improve the optical transmittance somewhat because of its lower density and index of refraction.

In the second stage of corrosion the silicate structure is attacked itself by hydroxyl ions which break down the siloxane bonds. The latter process becomes important in the case of basic solutions ($pH > 9$), in contact with the glass surface. In practical solar systems these second stage basic conditions could occur after repeated condensation of water on the inner side of a collector glass cover plate, but otherwise will rarely occur. Under normal dynamic run-off conditions, as in the case of vertical window glazing, a network dissolution will not take place, since the reaction products of the alkali-leaching process will continuously be carried off, preventing an increase in pH. The rate of weathering is determined largely by the inward diffusion of molecular water; it is therefore to a large extent a function of local climate and system conditions.

Weathering of float glass has been studied both after accelerated [6] [11] and natural [10] aging tests. Significant optical degradation has been observed after accelerated aging, involving exposure to constant relative humidity up to 100% at constant temperatures (50-70 ° C) and upon exposure to cyclic conditions. However, natural aging experiments show that surface weathering of soda-lime glass under normal, dynamic conditions does not result in severe optical degradation.

Table I: Material/load - Matrix

load / glass	1	2	3	4	5	6	7	8	9	10	11
A	5	1	5	1			6	3	3	7	6

A: Tempered low-iron, float glass.

Loads

1. Constant temperature
2. Cyclic temperature
3. Humidity
4. Condensation
5. Water bath/aqueous solution
6. Pollutants
7. Radiation (solar, UV, XE)
8. Combined indoor test procedures
9. Outdoor stagnation tests
10. Outdoor service conditions (natural aging)
11. Accelerated test conditions

Table II: Degradation mode/load-matrix.

Material: float, low-iron, tempered glass

	Load										
Degradation mode	1	2	3	4	5	6	7	8	9	10	11
weathering	4 6 11	6	4 6 11	11	7 9		2 3 4	2 3 4	2 3 4	1 2 3 4 13	2 3 4 11
stress corrosion/ strength reduction	5 8		5 8							10	
solarization							14 15 16			16 16	15

Number of reviewed publications: 16

Loads

1. Constant temperature
2. Cyclic temperature
3. Humidity
4. Condensation
5. Water bath/aqueous solution
6. Pollutants
7. Radiation (solar, UV, XE)
8. Combined indoor test procedures
9. Outdoor stagnation tests
10. Outdoor service conditions (natural aging)
11. Accelerated test conditions

2.2. Stress-Corrosion/Strength Reduction

Apart from optical degradation, strength reduction of glass can take place upon exposure to environmental in-service conditions [5], [8]. Generally, the strength of brittle materials like glass is reduced by surface flaws or cracks, which are introduced during manufacture, handling and through exposure to the environment (e.g. by abrasion). These flaws concentrate applied stresses and above a critical value of stress, fracture is initiated at the flaws. Besides, the reaction of atmospheric water present in the cracks with silicon oxygen bonds in the glass is accelerated by mechanical stresses at the crack tips. This phenomenon is called stress corrosion. Stress induced corrosion tends to weaken the glass further. Experimental strength tests with both new and naturally weathered glass plates showed that there was a significant decrease in strength associated with weathering [13].

2.3. Solarization

Solar-induced transmittance changes of glass are known as solarization. Solarization effects are mostly related to the iron content of glasses. Low-iron glasses with iron content less than 0.1% show hardly any solarization effects compared to glasses with larger iron concentrations. The iron impurities in glass are primarily Fe^{2+} and Fe^{3+} ions. The Fe^{3+} ion absorbs in the ultraviolet and is of little consequence to solar applications, except it does reduce the amount of ultraviolet light passing through the glazing. However, the Fe^{2+} ion has a broad absorption band around 1000nm, a spectral region in which the solar irradiance is considerable. Also, the $Fe^{2+} \rightarrow Fe^{3+}$ conversion reaction has been used to make higher transmitting float glass for reflectors.

Solarization of iron-containing glass is ascribed to solar induced changes in the Fe^{2+} absorption. Existing models are based on the redox reaction $Fe^{2+} \xrightarrow{h\nu} Fe^{3+} + e^{-}$, which is influenced by traces of Mn, As or Sb [14], but in many cases the exact mechanisms are not yet fully understood. Experimental accelerated solarization studies [15], [16] showed that solarization can result in both an increase and a decrease of the transmittance, dependent on the iron content and the glass type. Observed values for the changes in solar transmittance upon exposure to solar simulators range from an increase of 2.5% to a decrease of 5%. Furthermore, it was observed that the highest transmitting glasses did not show any noticable solarization effects.

3. Conclusion

It is concluded that the theoretical degradation mechanisms of float glass (weathering, stress-corrosion and solarization) are generally understood. Furthermore, natural aging experiments show that common float glass can be used adequately in most solar systems. The changes in optical transmittance due to weathering amount to a few percents at most. If high solar transmittance glazing is required, low-iron glass can be used which is not sensitive to solar-induced effects.

Therefore it is concluded that in IEA task X no further theoretical degradation studies on glass are necessary. Also, the establishment of some empirical guidelines to prevent weathering of glass in practical systems might be useful. However, a study of the decrease in transmittance due to dusting and cementation of particles might be relevant to determine long-term system performance variations.

4. References

NBS studies

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Solarization

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Degradation Modes of Polyethylene Terephthalate Used in Solar Applications

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1. Introduction

Polyethylene terephthalate (PET) is a condensation polymer that is used extensively as a packaging material and for window products. Reinforced PET resins for injection moulding are also available and specialty copolymers have been introduced.

Typical commercial PET resin melts at approximately 250 ° C. Oriented crystalline PET has good strength, toughness and clarity and resists weak acids, bases, and many solvents.[1]

The use of plastics for collector components is considered to reduce the cost. In fact, however, PET has been rather limitedly applied heretofore in the solar field,[2,3] except in the form of specialty films for glazing and passive cooling.

Therefore studies on the degradation mode of PET have scarcely been performed in the solar application and it seems that much that is unknown remains.

2. Photochemical Degradation

When a light-absorbing group in a polymer absorbs a photon, that group is raised to a higher energy level (excited state) which is usually a singlet state. The singlet may then undergo a process called intersystem crossing to give a triplet excited state. From these excited states several alternative events may occur. As the polymer molecule can dispose of the excitation energy in several nondegrading ways, only a small fraction of excited molecules will undergo degradation. The ratio of the number of molecules undergoing degradation to the number of quanta absorbed is called the quantum efficiency (θ) of degradation. In PET, the following value is recorded:[4]

$$\lambda \text{ max } 290{,}240 \text{ nm}; \theta \text{ at } 254 \text{ nm} > 1 \times 10^{-4}$$

most harmful λ, 280 – 360nm

PET is a polymer, in which the absorbing chromophore is part of the main chain; the ester carbonyl groups absorb light in the wavelength region of 280 - 400 nm. Exposure to light at 2537 and 3130 A in vacuum gave essentially the same results. Primarily on the basis of mass spectra of the volatile products and electron paramagnetic resonance spectra of the residual film, it was proposed that the major part of the chain scissions were due to the reaction in Figure 1.[5]

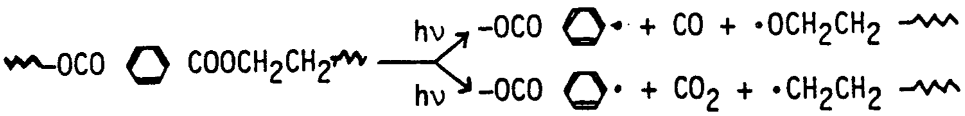

Figure 1

These do not represent primary photochemical changes but rather the earliest reactions deductible from the experimental observations.

Another paper reported on the photodegradation of PET film using spectrally dispersed light. The wavelength dependence of the increment, ΔA_{340} in the UV absorption spectra agreed well with that of ΔA_{3290} observed in IR absorption spectra. The latter has been known to be the evidence of the formation of -COOH end groups. Degradation mechanism differed with the wavelength.[6]

In the presence of air, photo-oxidative degradation involving hydroperoxide formation and cleavage takes place to form hydroxyl radicals and chain alkoxyl radicals which undergo several reactions leading to chain scission, the formation of monohydroxy terephthalate groups, and CO and CO_2 as volatile products.[7]

A few reports described the result of outdoor exposure. The PET sample showed a decrease in transmittance after 480 days exposure at Cape Canaveral, FL, USA. Microcracks on the surface were caused by both high humidity and high solar radiation, which resulted in the decrease of transmittance.[8]

3. Thermal Degradation[5]

The thermal degradation of PET is not important in its common commercial applications except under melt-spinning conditions. The pattern of thermal decomposition in PET has been carefully studied. At temperatures around 280 ° C, which are technically important in synthesis and fabrication, the primary reaction was the scission of ethylene ester to vinyl ester and carbonyl, which participated in subsequent reactions according to the reaction in Figure 2.

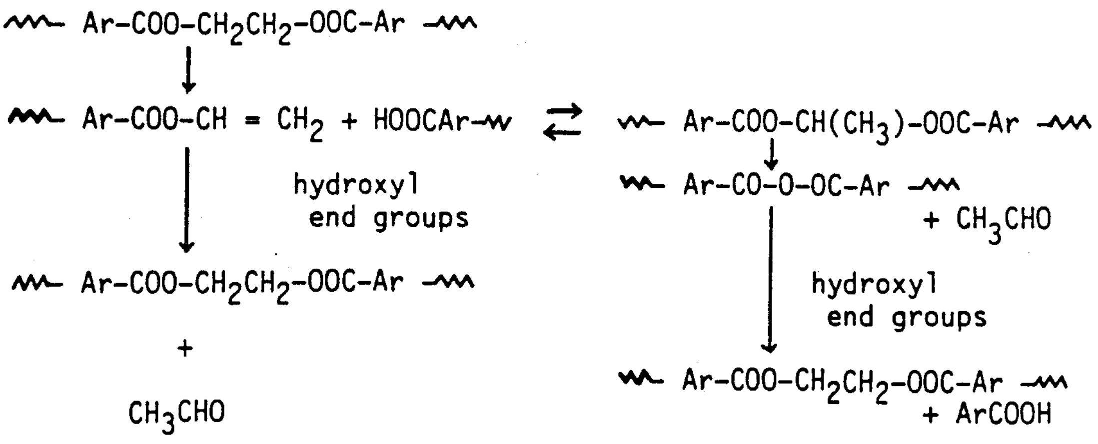

Figure 2

The most important effects were to produce (a) carboxyl end groups, which can affect the long-term stability of polyesters by autocatalyzing hydrolysis, (b) acetaldehyde, part of which can become involved in subsidiary reactions that may contribute to coloration in the polymer.[8]

Table 1 shows the gaseous products in the thermal decomposition of PET at 288 ° C.[9]

Table 1. Composition of Gaseous Product in the Thermal Decomposition of PET at 288 ° C[9]

Component	Mol % (to the total gaseous product)
CO	8.0
CO_2	8.7
H_2O	0.8
CH_3CHO	80.0
C_2H_4	2.0
2-methyldioxolane	0.4
CH_4	0.4
C_6H_6	0.4

4. Chemical Degradation[9]

The rate of hydrolysis of PET decreased when the film became thick, and on the films of a given thickness it differed with the relative humidity. By adsorption isotherm the rate was found to be proportional to the concentration of water in polymer.

In the hydrolysis of PET by acids, the order of feasibility to hydrolysis was: non-oriented and amorphous $>$ non-oriented and crystalline (48%) $>$ oriented and crystalline (38%). The rate of acidic hydrolysis of PET by HCl increased promptly at 3N concentration and the phenomenon was explained by the acid concentration in the polymer phase instead of that in aqueous solution phase; that is, only the undissociated HCl diffused into the polymer owing to its low dielectric constant and hydrogen ion did not enter into the polymer. When reaction proceeded the rate of hydrolysis was accelerated by the autocatalytic effect of carboxyl end groups.

The acidic hydrolysis (by 5N HCl at 70 ° C) or the hydrolysis at the neutral condition seemed to proceed randomly. But the hydrolysis by concentrated H_2SO_4 looked non-random because terephthalic acid was isolated in the initial stage of reaction.

Alkaline hydrolysis of PET (20% KOH solution at 98 ° C) was inhomogeneous concerning the polymer, which differed with neutral or acidic hydrolysis where the reaction proceeded homogeneously. By alkaline attack ethylene glycol and terephthalic (ester) ion appeared in the solution, and the weight decrease was observed, which showed that reaction occured at the surface. The result may be caused by the low permeability of OH^- ion into the polymer, owing to its low dielectric constant, and can also be supported by the repulsive effect of formed carboxylate ion against aggressive OH^- ion.

The decomposition of PET by methylamine aqueous solution took place by three stages. The initial degradation by methylamine occurred at amorphous phase, but little low molecular product was found. In the second stage the product became low molecular polymer, but the crystallinity of polymer rather increased. At the final stage the rate of decomposition reaction decreased gradually because the respective rates decreased in both amorphous and crystalline part.

For injection-moulded PET reinforced by short E-glass fibers, the general conclusion is that the acidic environment attacks the glass fibers while the alkaline environment attacks the PET matrix phase in a system of three composite layers across the thickness.[10]

5. Photostablization

Polymeric materials used in equipments for collecting solar energy must be photostabilized to be protected from harmful UV-rays. Much work has already been done to unravel the complexities of photooxidative processes and to develop some highly effective photostablizers and antioxidants which can delay the onset of embrittlement.[11]

A long lifetime can best be attained by immobilizing the stabilizer as part of the molecular structure. Not so many works, however, have been performed yet along this line.[12] The compound as 2(2,4-dihydroxyphenyl) 2H-4-hydroxybenzotriazole, has been shown to have a potential as a polymer-bound stabilizer for polyesters.[13]

6. Conclusion

As a polymer which has an absorbing chromophore in its main chain, the degradation of PET at outdoor conditions should be studied more elaborately if we desire to use more PET for solar field, because not so much work has been carried out to date.

On the other hand, the thermal degradation of PET has been well studied comparatively. In fact, however, the practically important problem is the autocatalytical thermal oxidative degradation initiated by solar rays rather than purely thermal degradation, and we could not find any instructive documents on this matter. As a condensation polymer, PET naturally seems to suffer from the effect of humidity and air pollutants.

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Failure and Degradation Modes of Sealants for Insulating Glazings

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1. Introduction

Insulating glass glazings are generally adopted in the building industry. The advantages are evident: energy savings and better comfort in winter. Special products with low-emittance coatings are being marketed with improved performance characteristics, and combinations with laminated glass show excellent acoustical characteristics. But even with these advantages, insulating glass has introduced durability questions. In single glass glazing, the main degradation mode consists of weathering of the outer glass surface. The degradation of insulating glass glazing is more complex. In this chapter a summary will be given for the main degradation and failure modes noted for insulating glazings.

We confine this discussion to the dual organic polymeric sealed insulating glass glazings, composed of two sheets of glass, a metal spacer and two different sealants. The sealants consist of a primary sealant of polyisobutylene used between the spacer and the glass edges. The secondary sealant is used in the joint between the glass edges and the back of the spacer. The primary sealant is the main barrier for moisture penetration, and the secondary sealant is the main barrier against attack by atmospheric and chemical agencies.

Also a molecular sieve desiccant is used in the spacer. It provides a dry air space and a buffer for water vapor diffusion through the edge seal to further extend the lifetime of the insulating glass unit. This system is common in Europe and is being used in the United States. This glazing system is an interesting field of study and not yet fully understood from the viewpoint of stability and degradation. Also, in this study some attention will be paid to the other insulating glass systems such as all-glass sealed edge, soldered edge and single organic polymer barrier systems.

The degradation of insulating glass glazings strongly depends on the quality of the glazing. Such factors as improper design and the setting of glazing materials with linseed oil putty have a negative impact on the lifetime of a glazing system. The proper design of insulated glass glazings has been detailed by other authors [1-5]. The aspects of durability of insulated glazings have several references [6-9]. During this discussion of degradation modes of insulating glass, aspects of improper glazing will not be considered.

2. Failure and Degradation Modes

2.1 Water Penetration and Dew Point

The main degradation mode of insulating glass is by water vapor or water penetration through the edge seal into the airspace gap. The air space is filled with dry air and usually a desiccant is used as a buffer for possible water penetration. Nowadays, most molecular sieves are used as the desiccant. They have high adsorbtion capacity and extremely low dew points [10-13]. But if the humidity in the air space becomes too high due to saturation of the desiccant, then internal condensation is expected when the glass temperature drops below the dew point in the air space. Condensation leads to the deposition of alkali salts on the inner side of the outer glazing which is inaccessible for cleaning, so that clear view is disturbed and the unit has to be replaced. Some manufacturers claim methods to clean the internal glass surfaces by water spraying through bored holes in the glass, thus creating a regular double-glazed window. Experience has shown that after such a treatment deposition of salt still occurs. The dew point in the air space can be used as a measure of the quality of the insulating glass unit and a measure of risk of condensation. There are special dew point meters for this purpose. [5] The highest permissable dew points in insulating glass depend on the glass temperature in winter. The dew point is determined by the minimum glass temperatures. In Holland the maximum dew point of -5 ° C (sea climate!) is seen, but in other northern European countries -10 ° C is seen. The end of the life of an insulating glass unit may be determined as when the humidity within the units reaches these levels. On the basis of humidity levels, dew points and the related water vapor pressure and the maximum permissable water content of the desiccant within the unit can be calculated. To do so the relationship between dew point and water content of the desiccant must be known. Thus the amount of water penetration can be calculated, which is of help for evaluation of durability tests and life time prediction [10].

This is done for a dual organic sealed glass edge, resulting in life times of hundreds of years (!). But this is pure theory; in practice the edge seal is subject to all kinds of degradation modes, affecting the water vapor resistance and undermining this theory. In the next section, the different degradation modes will be discussed.

2.2 Mechanical Strains

Insulating glass is subject to pressure variations by wind load, barometric pressure, and temperature variations of the enclosed air. Temperature differences between both lights induce shear stresses. All these modes affect mechanical forces on the glass edges and thus on the edge seal, with the risk of fatigue of the sealant and the bond to glass, and deterioration of the water vapor resistance. The degradation of the dual organic edge seal mainly consists of degradation of the butyl barrier, the main barrier for water vapor penetration in this system, and is caused by the s.c. pumping effect. The pumping effect is the continuous movement of the glass edges under the influence of the abovementioned climatical strains. By the pumping effect the butyl barrier gradually deforms, finally resulting in the following degradation modes:

a. stretching of butyl barrier
b. adhesion loss of butyl from glass
c. adhesion loss of butyl from space or
d. cohesion loss

Which mode dominates, depends on characteristics of the butyl sealant (plasticity, adhesion strength). Any degradation of the butyl barrier has a negative impact on the water vapor resistance of the edge seal. How much depends on the water vapor characteristics of the secondary outer seal. This argues for a better water vapor resistance secondary sealant like polysulfide; the outer sealant material from the very beginning in the history of insulating glass. Leaks in the butyl barrier are well set off by the polysulfide. Polyurethane is a substituent for polysulfide, with comparable water vapor resistance characteristics.

Water vapor resistances of silicon rubbers vary; newer products, specially developed for application as secondary sealants in insulating glass, do meet requirements. But not only water vapor resistance of the secondary sealant is important but also the elasticity and adhesion strength to glass and spacer.

The secondary sealant must guarantee a certain stiffness of the edge seal to minimize the movement of the glass edges (pumping effect) and the degradation of the primary sealant. The stated mechanical loads also have an impact on the secondary sealant; fatigue of the bond to glass and of the material itself, resulting in adhesion or cohesion failure. The stiffer the secondary sealant, the higher the stresses at the interface sealant - glass, and risk of failure. Adhesion failure and leaks in the secondary sealant may temporarily be set off by the primary barrier, but sooner or later lead to failure of the insulating glass. Thus the modulus of the secondary sealant must be a good compromise. In mono organic edge seals, like hot melt systems, adhesion loss leads to immediate failure.

2.3 Photochemical Degradation

Solar radiation, especially short-wave radiant ultraviolet (UV), initiates photochemical reactions in the organic sealants: disintegration of polymers and all kinds of by-reactions like oxidation [14, 15]. Even partly covered by the rebate, in the course of years a considerable amount of UV-radiation reaches the susceptible interface; secondary sealant-glass, via internal reflection. Data about solar radiation are available for different countries [16,17]. The photochemical reactions have a negative impact on the mechanical properties, especially the bonding to glass. Typical degradation effects are: discoloration, loss of adhesion, even adhesion failure.

Of the applied secondary sealants in organic sealed insulating glass, silicon rubber has the best characteristics as to photochemical attack. Polysulfide and polyurethane are more or less susceptible to photochemical degradation, and thus ask for adequate depth of the rebate for protection against solar radiation.

Sealants of the butyl type are relatively resistant to photochemical degradation. More data about sealants can be found in Refs. [18 - 21].

2.4 Chemical Degradation

When watertightness of the glazing is insufficient, rain water containing contaminants from the air--like sea salts and acids--penetrates into the rebate and affects the secondary sealant, especially the interface, as sealant-glass is susceptible to chemical attack by water.

Continuous contact of sealants with water must be avoided as much as possible by proper draining and ventilation. Also, glazing compounds must be compatible with the secondary insulating glass sealants.

2.5 Remaining Degradation Modes

Fogging

A degradation mode of a different type is the deposition of organic consistuents from the organic sealants onto the inter sides of the glass, the so-called "fogging". This disturbs the clear view and urges for replacement of the unit. Fogging is caused by the UV-radiation of the sun.

Glass breakage

A considerable percentage of failure in practice has to do with glass breakage. Glass breakage may have different causes including the following:

- weakening of the glass edge by improper handling
- mechanical stress by improper setting and glazing
- thermal stress by temperature differences between glass center and glass edge

Sun shading glasses and those with low-emittance coatings are especially susceptible to thermal stress.

Special glasses

Special insulating glasses such as [1] insulating glass with low-emittance coating and/or special gas filling for better U-value and [2] combinations with laminated glass for acoustic or safety aims, introduce extra degradation modes like degradation of the coating, and problems of adhesion of the sealants onto the coated glass (soft coatings have to be removed from glass edges), gas leaks, deterioration of the interlayer, etc.

3. Conclusion

The degradation of insulating glass is a combined action of the different climatical agencies: wind, barometric pressure and temperature variations, solar radiation, rain, and glazing conditions. The failure mechanism consists of the forming of a deposition of contaminants on the inaccessible inner glass surfaces that disturbs the clear view and urges for replacement of the insulating glass unit although thermal and acoustical properties are not deteriorated. The degradation of dual-sealed insulating glass is very complex and not yet fully understood. Better study must be made of the loads in practice for different glazing conditions, locations, dimensions of glass units, and interactions of stiffness of glass and rebate. Solar radiation, thermal and wind load must be considered; they are insufficiently dealt with in current durability tests.

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Stability and Durability of Electrochromic Switching Films for Glazings

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1. Introduction

There is considerable interest in the research and development of materials and devices that can be used for optical switching of large scale glazings. The ability to optically switch a glazing has great potential benefit to the building aperture. It can offer dynamic control of both daylighting, solar energy for heating and regulation of solar radiation for the reduction of air conditioning load. There are several potential switching technologies for glazings, including electrochromism, thermochromism, photochromism, liquid crystals and physio-optic phenomena. One of the most promising technologies for optical switching is electrochromism.[1,2] This study is confined to the discussion of electrochromism.

However, electrochromism with its great potential has its share of technical uncertainties and problems. A few prominent effects are seen in many different devices namely, residual coloration, loss of dynamic range and stability of the device during long term cyclic switching. The origins of the effects are only partially understood at this time. Also, it is very important to note that these effects are dependent upon the conditions of testing and in some cases are not permanent. Even though it is early to discuss these problems while the research on devices moves forward, it is important to discuss some of the observations obtained. With this study we hope to gain a better understanding of stability in these devices and to comment on test methods used, lifetime and performance criteria for electrochromic optical switching films.

The following work is a composite of several researchers reported data including the research of the author and his observations of the field. The following findings are sketchy but they serve to begin the process of analysis. Some of this information cuts across all the subtasks A-D in the International Energy Agency, IEA Task X- Solar Materials. Subtask A is Performance Criteria, B is Test Methods, C is Lifetime Prediction and D is Failure and Degradation of materials. It is important to consider the aspects of all these topical areas because material performance and stability is an important function of the test and exposure conditions.

2. Performance Criteria and Device Design

Before we can fully understand the issues of stability we must define the performance criteria and introduce the design of electrochromic devices. The potential performance of an electrochromic device is estimated as the following:

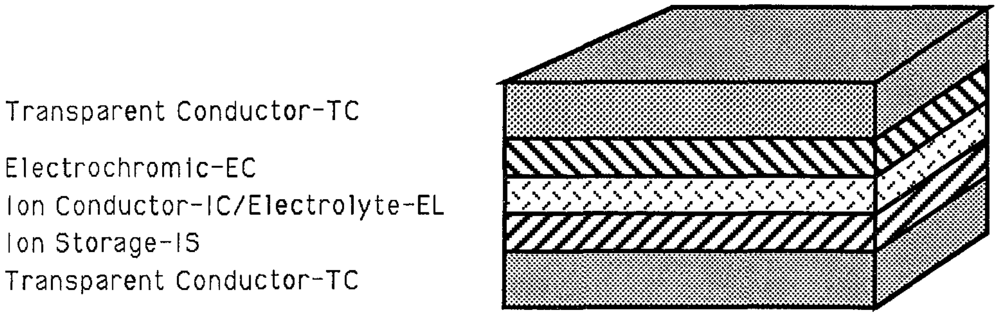
SPECTRAL RESPONSE	
Solar Control	T_s (BLEACHED) = 50-70% T_s (COLORED) = 10-20%
Visible Control	T_p (BLEACHED) = 50-70% T_p (COLORED) =<10-20%
Near-IR Control	R_{nir} (BLEACHED)=10-20% R_{nir} (COLORED) =>70%
SWITCHING VOLTAGE	1-3 VOLTS (Small Device) 10-24 VOLTS (Large Device)
MEMORY	1-12 HOURS
CYCLIC LIFETIME	>10K-1M CYCLES
LIFETIME	5-20 YEARS
OPERATING TEMPERATURE	-30 to 70°C 0-70°C, If Protected

This performance criteria was obtained from collected data from several researchers and by best estimates of the necessary requirements for a building window glazing. The actual application of the switching device may vary from these idealized values. For example, in automotive applications an electrochromic device is expected to operate at higher temperatures than for a building application.

The upper use temperature might be as high as 80-90°C, but the required lifetime might be only 7 years. Also, for a sunroof application the amount of UV radiation is higher than for vertical glazing. The optical values of this data reflect the performance of the entire device. The bleached transmission properties are limited by the optical properties of the transparent conductor and substrate material. Two transparent conductors on glass without the electrochromic layers can drop the maximum solar transmittance to about 72-56% depending on the material.[3] Because of this, improvements in transparent conductors are also important to the performance of electrochromic devices. Furthermore, for large scale application transparent conductors must have very low sheet resistances to overcome resistive power loss and slow switching time.

Electrochromic devices function by the reversible injection/ejection of both electrons and ions in/out of an electrochromic material. A typical electrochromic reaction for a cathodic coloring material is : $a\text{-}WO_3 + xH^+ + e^- \leftrightarrow a\text{-}M_xWO_3$, $M = Li^+, H^+, Na^+$, etc., where WO_3 is transparent and M_xWO_3 is blue colored. A typical anodic coloration reaction is: $Ni(OH)_2 \leftrightarrow NiOOH + H^+ + e^-$, where $Ni(OH)_2$ is transparent and NiOOH is bronze colored. Devices are designed in such away to store ions and shuttle them back and forth into the electrochromic layer with applied potential.

To understand how devices degrade and fail we must discuss the structure and materials of different devices. The electrochromic device is composed of generally 4–5 layers. There are three general structural types, designated as Types A–C in Figure 1. The structure of Type A begins with a transparent electronic conductor layer on a glass substrate. Typically this conductor is indium tin oxide, In_2O_3:Sn (ITO) or tin oxide doped with antimony or fluorine, SnO_2:Sb or SnO_2:F. The second layer is the electrochromic layer. It has both ionic and electronic conduction. The typical electrochromic layer can be amorphous or



Type A Combined Storage and Conductor	TC	EC	IC	IS-TC	
Type B Ion Storage Layer Device	TC	EC	IC	IS	TC
Type C Complementary Electrochromic	TC	EC	IC	EC	TC

Figure 1. Schematic cross section depicting generalized electrochromic device structures.

crystalline tungsten oxide, a-WO_3 or c-WO_3, iridium hydroxide, Ir(OH) or nickel hydroxide, $Ni(OH)_2$. The most used material is a-WO_3. The third layer can be an ion conductor or an electrolytic material. This layer exhibits ionic conduction. The fourth layer is the counter electrode material. When an electrolyte is used, with sufficient ion storage, the fourth layer is not needed. In Type B, the fourth layer is a combined electronic conductor and ionic storage media, thus eliminating the fifth layer. The fifth layer is the second electronic conduction layer, similar to the first layer. Three types of structures can be seen. Type C is known as the complementary device structure where the counter electrode and working electrode are both electrochromic materials, one coloring anodically and the other cathodically. In such a fashion they color together and bleach together. By use of two electrochromic materials one can increase the optical density of the device over that of the single material. For example this is done in the Nissan device.[4] In this device cathodic a-WO_3 and anodic Prussian Blue, $(Fe_4(Fe(CN))_6)_3$ are coupled together. But by doing so they introduce an electrochemical imbalance. To make a practical device another electrode must be added to periodically adjust for the charge imbalance in the device. Probably the most successful complementary device is based on anodic IrO_2 or $Ir(OH)_2$ and cathodic a-WO_3. An example of this device has been made by EIC Labs.[5]

3. Test Methods for Electrochromic Devices

A number of test methods are used for the analysis of electrochromic devices. All of the methods known are not standardized for the testing of electrochromic devices. The type of methods used are: (1) cyclic voltammetry cycling-accelerated test; (2) square wave cycling-accelerated test; (3) solar and outdoor exposure; and (4) accelerated UV and Weather-O-Meter exposure. Cyclic voltammetry is a measure of the cyclic current and voltage response of the device. A triangle potential is used as the driving potential (usually under +/-2V) and a reference electrode is used to help correlate potentials to known electrochemical processes. Cyclic voltammetry is very good for determination of chemical changes in the electrode as it cycles. In general, a d.c. voltage is used to drive actual devices. Square wave cycling is used to simulate an accelerated cyclic d.c. potential response. However since electrochromism is actually a current controlled phenomena, current sources with controlled voltage have also been used for testing.[6] Accelerated UV exposure is accomplished by the use of specialized high intensity lamps.[7,8] Care must be taken not to thermally effect the device when this test is performed. All of these methods are coupled with standard tests of spectral transmittance, reflectance and integrated optical properties.

Examples of idealized responses for cathodic and anodic type electrochromic devices are shown in Figures 2 and 3. A measure of performance is the coloration efficiency (CE) expressed as cm^2/C. To obtain this value the total injected/ejected charge as a function of unit area must be known. This information can be obtained by integration of voltammetry data or by the use of a coulomb meter. Information on the amount of charge required for

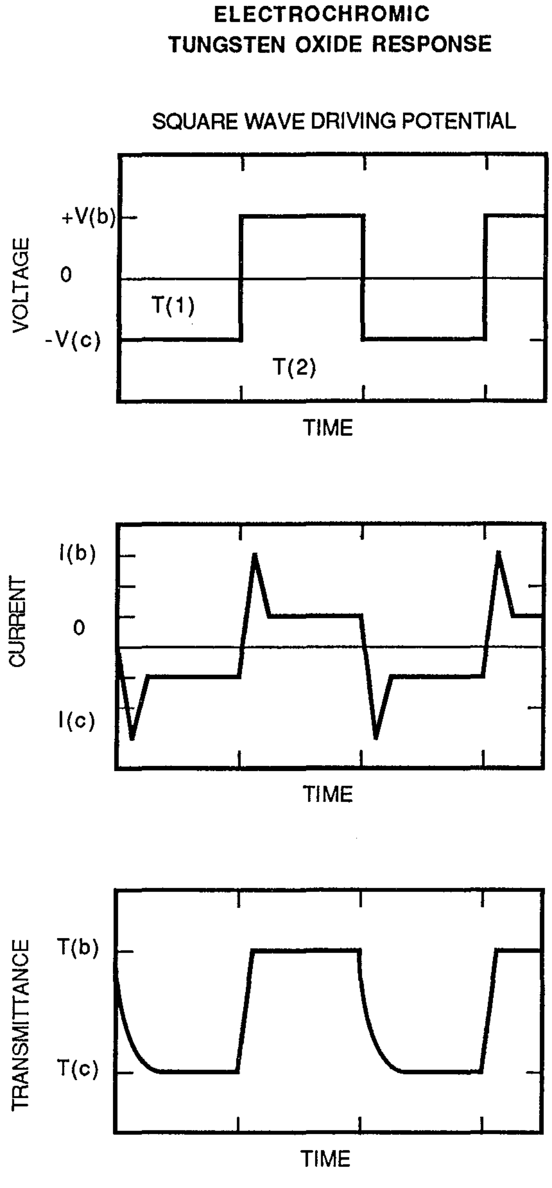


Figure 2. Response of an idealized electrochromic tungsten oxide switching device. Shown are the driving potential and current with resulting transmittance response.

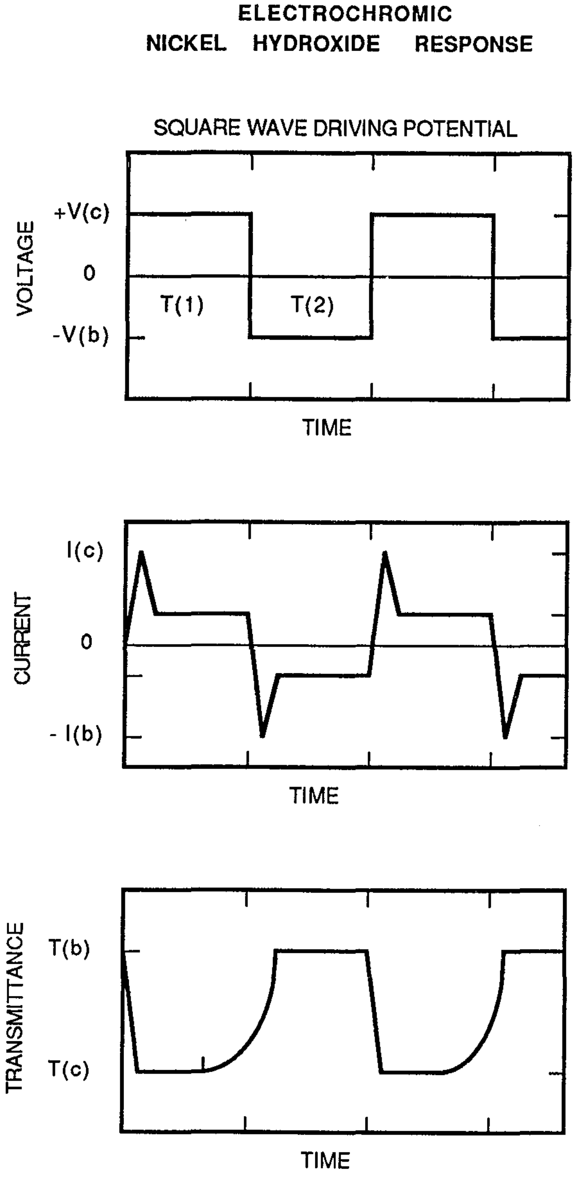


Figure 3. Response of an idealized electrochromic nickel oxide switching device. Shown are the driving potential and current with resulting transmittance response.

coloration compared to bleaching will also give the efficiency of each half cycle. The change in surface density of charge, mC/cm^2 (also many authors referred to this quantity as charge, charge capacity or charge per unit area) is monitored during cyclic testing. In some cases the coloration and the bleaching cycle require different amounts of charge to give the same change in optical density. Also, the rates at which a device colors and bleaches are usually different.

The change in optical density (ΔOD(w) can be obtained from the relationship between injected charge (Q) and the coloration efficiency: $\Delta OD(w)=Q/CE(w)$. Where both CE(w) and OD(w) are wavelength (w) dependent quantities. Also, optical density can be obtained by $\Delta OD(w)=\log(T_b(w)/T_c(w))$, where $T_b(w)$ is the bleached transmittance and $T_c(w)$ is the colored transmittance. Also, for transparent devices the absolute values of optical density need to be given, defined as: $OD=\log(T_o/T_x)$, where T_o is the incident or reference transmittance and T_x is the measured transmittance value of the device. Because we are interested in the modification of the photopic and solar spectra, both spectral and integrated data should be reported. Frequently for display device studies, only contrast ratios or the change in optical density are given.

4. Device Lifetime and Degradation Modes

A few degradation and ageing mechanisms have been identified in electrochromic devices. The mechanisms are film dissolution, cyclic electrochemical instability, transparent conductor etching, gas generation, humidity dependence, secondary reactions and photoreactions. Some of the mechanisms identified are specific to the materials, device design, and the operating conditions used. The most is known about amorphous tungsten oxide and its use in devices. There is a lot of information about this material because of its development for small display devices during in the 1970's. Many of the degradation mechanisms identified can be avoided or controlled by proper design and operating conditions. But, one must be careful when applying those findings to transparent devices with new counter-electrodes, larger areas and slower switching requirements.

4.1 Film Dissolution

One effect that has been noted by many authors is the dissolution of a-WO_3 films in water and to some degree in acidic environments, following the reaction: a-$WO_3 + 6h^+ \leftrightarrow W^{+6}$(solution) + $3/2O_2$. The dissolution of c-WO_3 is considerably slower. The dissolution rate of a-WO_3 in water has been estimated as 2.5 μm/day.[9] The dissolution rate (R) is a function of the electrolyte pH. For example the rate is 1μm/yr at pH=0 and and 10^3 μm/yr at pH=6, following the equation $R= k_1 10^{0.33pH}$. At higher pH values the rate increases, for a pH=9 the rate is 10^4μm/yr, following the equation $R= k_2 10^{0.66pH}$. These values were obtained for a flowing electrolyte.[10] For a static sealed electrolyte these rates decreased by an order of magnitude to 2-2.5 nm/day at 50°C in a glycerin-H_2SO_4.[9] This effect can pose a shelf-life problem for these devices. It is thought that a-WO_3 films are in the form of trimeric clusters which are weakly bound to each other with water bridge bonds. This results in a very open microstructure and high proton mobilities, giving higher switching speeds. This structure has been identified as the xerogel structure, consisting of a highly porous low density oxide.[11]

Unfortunately this structure is subject to dissolution and cyclic errosion. When the film dissolves it forms metatungstate or polytungstate ions.[12] To reduce this problem, alkali salts in aprotic (non-aqueous) electrolytes have been used, but the drawback is that the device response is decreased.

4.2 Cyclic Stability

Another degradation mechanism appears during cycling. Typically during cycling, the larger the change in coloration is, the shorter the lifetime of the device. Experimental derived results are shown in Figure 4, after work done at RCA on a-WO_3 display devices.[10] This mechanism of degradation is not fully understood, but it appears fundamental in many devices. But the degree of degradation is very dependent on electrolyte type and operating conditions. From the RCA work, if a device is to last 10^6 cycles then its contrast ratio must be within the range of 2:1 to 4:1 ratio. The contrast ratio is defined in the RCA study as the ratio of reflectances compared to a white background as: $CR(w) = R_b(w)/R_c(w)$, where $R_b(w)$ is the reflectance in the bleached state and $R_c(w)$ is the reflectance in the colored state. Work on protonic devices has suggested that cyclic degradation is an extension of the dissolution process or voltage enhanced corrosion.[12] In protonic devices that have been cycled for many thousands of cycles and dissembled, the a-WO_3 film has been found to be granular and is less adherent to the substrate.[9] It is suspected that the film has suffered mechanically from hydrogen embrittlement. The most obvious change during cycling is the gradual reduction of charge per unit area during bleaching and coloration of the film. This results in a decline of the change in film's optical density.

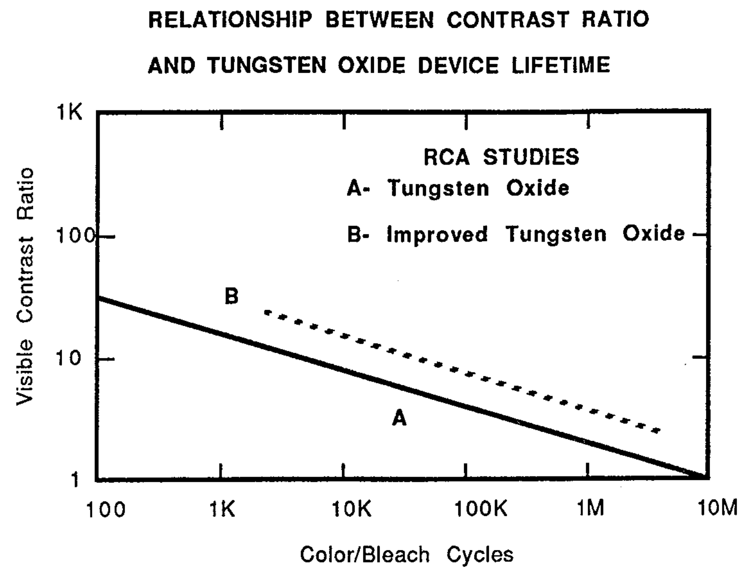


Figure 4. Relationship between contrast ratio and lifetime for a tungsten oxide electrochromic device (ITO/a-WO_3/ electrolyte /metal). Two device responses are shown: (A) standard vacuum evaporated film and (B) films produced by an improved process From the RCA work.[10]

In so-called aprotic systems, a-WO_3 corrosion is slowed by two processes: (1) low ionizability of large organic molecules, and (2) inhibited tungsten ion formation. For a-WO_3 electrodes cycled in $LiClO_4$- propylene carbonate (PC) after 10,000 cycles of coloration and bleaching, a decrease in injected charge density is noted. The charge density began at 5-6 mC/cm^2 and dropped to 4-1 mC/cm^2 after $5x10^5$ cycles. An example of this is shown in Figure 5. Only an electrochemical emf change was noted in the film. After cycling, Li ions were found bound into the film structure and were judged responsible for the emf shift but not active in coloration. After cycling, the film in the bleached state becomes more ion conductive as the result of Li incorporation.[14-18] There appear to be two active sites for lithium ions one for coloration: $a\text{-}WO_3 + xLi^+ + xe^- \leftrightarrow a\text{-}Li_xWO_3$ and another for ion exchange according to: $W\text{-}O\text{-}H + Li^+ \leftrightarrow W\text{-}O\text{-}Li + H^+$. Also the O/W ratio increased during cycling. This result may mean that the a-WO_3 may form a metatungstate structure $(M^+)_6(W_{12}O_{39})$ where M = H, Li, etc., which can serve as an ion exchange site.[15] A decay factor of two in charge has been noted after 100 hours of cycling ($9x10^4$ cycles) of a a-WO_3/$LiClO_4$-PC /Li_xWO_3 device.[13] It was found that by irradiating the cell with UV light while applying a bleaching voltage the decline in the charge injection level was reduced.[13]

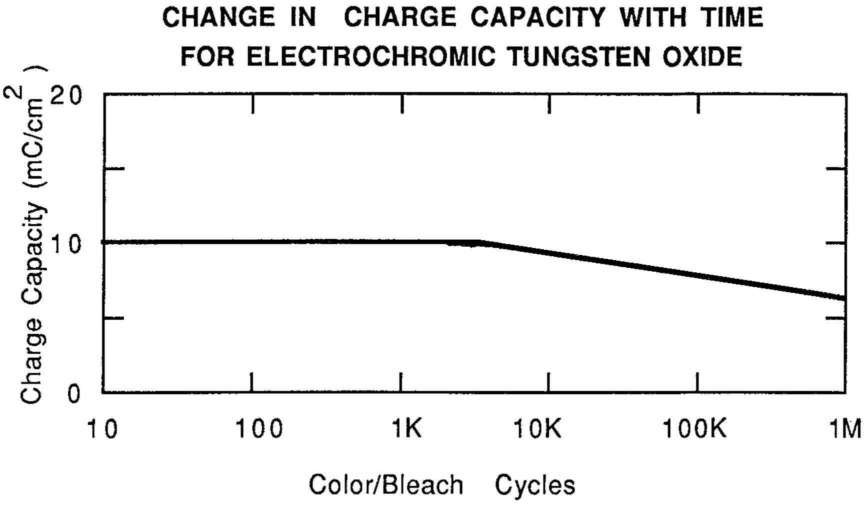


Figure 5. Long term cycling of tungsten oxide devices (ITO/a-WO_3/$LiClO_4$+Redox/ITO). The decline in charge capacity (charge per unit area) and hence optical density can be seen after long cycling. This effect is seen in many device types. After the Asahi Glass work[14-17].

Preliminary work on the cycling of sputtered electrochromic $Ni(OH)_2$ has shown only a small change in the transmittance after 10^4 cycles.[19] Work on cathodic electrochemically deposited $Ni(OH)_2$ has shown early residual coloration after cycling.[20] But work on anodically deposited $Ni(OH)_2$ films and devices has shown good stability.[21-23]

4.3 Transparent Conductor Etching

Another degradation effect occurs when the electrolyte chemically etches the transparent conductor layer . The transparent conductor In_2O_3:Sn (ITO) has some of the best optical and conduction properties is sensitive to etching in acids. ITO has a reduction potential of -1.0 V to -2.5V (SCE) depending on the pH of the electrolyte.[17] ITO can go through electrochemical reduction by: $I\ n_2O_3 \rightarrow 2In^{+3} + 3/2O_2 + 3e^-$. Doped SnO_2 has much better etch resistance, but does not have as good optical and electrical properties as ITO [3] However, in strong acids doped SnO_2 can go through electrochemical reduction by [9]: $SnO_2 \rightarrow Sn^{+4} + O_2 + 4e^-$.

In the SnO_2/a-WO_3/P-AMPS/C device, the reduction of SnO_2 is seen at potentials above 1.0V. To cure this problem a protective over can be used for areas in direct contact with the acidic electrolyte.[6]

4.4 Gas Generation

A very serious device degradation and failure effect is internal generation of gas. For a-WO_3 devices there is a danger of generating H_2 gas if the voltage across the device is too high. Also, if the a-WO_3 film is colored to H_xWO_3 beyond $x \approx 0.28$, then an electrode-electrolyte interface reaction can occur causing dissolution of H_xWO_3 and formation of H_2 gas.[10]

In ITO/ a-WO_3 /IC/Au devices it has been concluded that water in the device is dissociated at the Au interface during coloration. During bleaching gas bubbles are observed at the Au interface during application of a -1V potential.[24] For electrochromic TiO_2 the coloration peak occurs after the oxygen evolution potential. This makes TiO_2 impractical for use with water based electrolytes because of gas generation.

4.5 Water and Humidity Dependency

Another important effect occurs in ITO/ a-WO_3 /IC/Au devices. These devices have been reported to be very dependent upon ambient humidity. Experiments have shown that weight changes occur during coloration and bleaching which correspond to adsorption and desorption of water in the cell and its surroundings. Mass spectrometer measurements have shown that O_2 left the cell during coloration and H_2 left the cell during bleaching. Also, coloration does not occur until a threshold voltage (which corresponds to the electrolysis of water) is reached across the insulating layer. This electric field disassociates the water in the insulating layer thereby providing the necessary protons for coloration.[25-27]

The coloration and bleaching process was studied in a ITO/a-WO_3 /a-SiO_2/Au device.[28,29] The gold interface serves as a surface for catalytic dissociation of water. When the device voltage exceeds 1.3V, a hydroxide layer is formed on the gold surface following: $Au + 3OH^- \rightarrow Au(OH)_3 + 3e^-$. At this stage coloration takes place in the a-WO_3 layer. Above 1.6V the threshold for oxygen discharge is reached. On the negative current cycle, at 0.8 V the reduction of gold hydroxide occurs and bleaching begins. At -0.1V water is reformed. Final bleaching of the a-WO_3 film is observed at -0.4V. At -3V oxygen evolution occurs. The presence of water in this device is important to its operation and the gold layer serves as a catalytic surface.

4.6 Secondary Reactions

The organic viologen system has always been attractive for switching devices because its absorption spectrum can be adjusted at any visible wavelength, it has high charge efficiency (2.5x better than WO_3) and switches fast. The problem with the viologens is that they show unexpected secondary irreversible reactions with use.[30] These reactions is are seen in conjunction with liquid electroytes, there is a possibility of suppression with solid electroytes.[31]

4.7 Photoreactions

It is known that a-WO_3 is photochromic when exposed to UV radiation.[7,8] The photocurrent rises dramatically for wavelengths below 400 nm. Also, for annealed films the photocurrent rises between 400-480 nm.[7] It has been observed that in a-WO_3, $W^{+6} \rightarrow W^{+5}$ under irradiation of UV light at 253 nm in vacuum at RT.[8] This means that an electrochromic device based on a-WO_3 will have its bleaching and coloration kinetics slowed down by the effect of photochromism. This is one reason why indoor and outdoor tests give different rate kinetics.[16] After 100 hours of UV irradiation in a Weather-O-Meter at 63°C, the injected charge dropped from 13 to 8 mC/m^2.

Photochromism can be used to regenerate aged a-WO_3 devices. After long cycling the electrochromic layer or electrolyte contains trapped charge, which causes the charge injection levels to fall, and an emf shift is noted of -170mV. A contrast ratio of 4:1 was seen before cycling. The peak current density was 4 mA/cm^2 bleached and -5 mA/cm^2 colored. After 100 hrs ($9x10^4$ cycles) the peak current was 1 mA/cm^2 bleached and -4 mA/cm^2 colored. After UV regeneration the bleaching current became 2 mA/cm^2 and -5 mA/cm^2 colored. By irradiation and biasing the device in the bleached state the energy of UV light freed trapped charge and partially restored the dynamics of the uncycled device.[13]

4.8 Thermal Dependence and Decomposition

The thermal dependence of cyclic switching is important to the lifetime of the electrochromic device. A device consisting of Glass/ITO/a-WO_3/$LiClO_4$- Redox/ITO/glass have been studied for thermal ageing.[16,17] As depicted in Figure 6, color/bleaching cycles were carried out using a D.C. potential of 1.0V or-1.0V for a 1 min. interval. Over 10^5 cycles were performed on the device. Cells were cycled for over 30 days under different

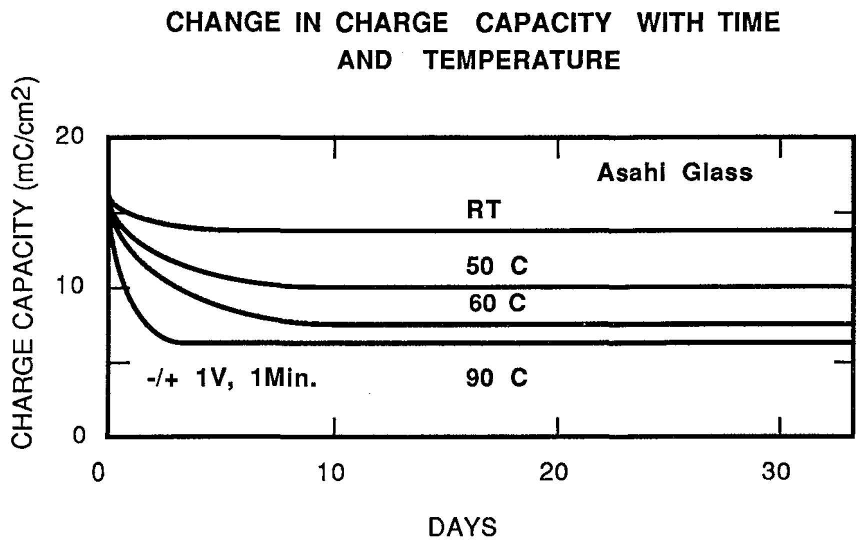


Figure 6. The decline in charge capacity (charge per unit area) with time and temperature for a tungsten oxide electrochromic device (ITO/a-WO_3/$LiClO_4$ +Redox /ITO). This device was cycled at +/- 1V potential for 1 minute intervals over the period of testing. After the Asahi Glass work.[14-17]

temperatures of, RT, 50, 60, 90°C. The effect of higher temperature caused the device to slow down and decline in charge injection levels. After a few days a constant charge injection level was achieved. The injected charge per unit area starts at about 16 mC/cm^2 and drops to 14 mC/cm^2 at RT. At 90°C the injected charge drops and becomes constant at 6 mC/cm^2.

Thermal stability is important for devices with polymer electrolytes. Studies have been performed on the $LiClO_4$-PC elctrolyte.[4] Decomposition was noted at 10^3 hours at 60°C, $3x10^2$ hours at 70°C , $2x10^2$ hours at 80°C and 15 hours at 90°C. It is also common for gas bubbles to form in the device during decomposition.

4.9 Device/ Load and Degradation Mode/Load Matrices

The following matrices detail the cited references in terms of tests and resulting degradation modes detected. Only the cases cited in the references are tabulated; in a few cases further testing was done but not reported in the open literature. Additional data for selected investigations are detailed in the Appendix.

Materials/Load Matrix

The following matrix shows the types of electrochromic devices that have been studied for stability and durability. The types of loads or stresses are indicated from 1-8.

Materials	1	2	3	4	5	6	7	8
A	14-16,17	14-16,17		15-17	15-17	15-17	15, 16	14
B	13	13		13				
C	18	13		13				
D	4	4		4			4	
E	5							
F	6	6						6
G	9, 11, 12	9					9, 12	9, 11, 12
H	24, 27		24, 27				27	24, 25
I	25, 28, 29							28, 29
J	19-23							
K				7, 8			7, 8	
L	30							

Device Types	**Load Type**
A. ITO/a-WO_3/$LiClO_4$+Redox/ITO,Metal	1. Cyclic Volt./Current
B. SnO_2/a-WO_3/$LiClO_4$+PC/ $LiWO_3$/SnO_2	2. Temperature
C. ITO/a-WO_3/$LiClO_4$+PC/Metal	3. Humidity
D. SnO_2/a-WO_3/$LiClO_4$+PC/ Prussian Blue/SnO_2	4. UV Radiation
E. ITO/a-WO_3/Poly-AMPS/a-IrO_2/ITO	5. Outdoor Exposure
F. SnO_2/a-WO_3/Poly-AMPS/Carbon	6. Weather-O-Meter
G. SnO_2/a-WO_3/Electrolyte/Metal	7. Static Conditions
H. ITO, SnO_2/a-WO_3/MgF_2,LiF/Au	8. Internal Water
I. ITO/a-WO_3/a-SiO_2/Au	
J. ITO,SnO_2/$Ni(OH)_2$/KOH/Pt	
K. a-WO_3, a-MoO_3	
L. ITO/Viologen/Metal	

Degradation Mode/ Load Matrix

This matrix compares the type of load or stress applied to the electrochromic device or material to the resulting degradation or aging mode.

Deg. Mode	1	2	3	4	5	6	7	8
A	9, 10, 12, 18	9, 10					9, 12	9, 10
B	5,10-13,18, 20					16-17		14
C	14-18							
D	9							
E	6, 17						9	
F	10, 24	4						
G	25-29		25-27					25-29
H	30			13,16-18				
I	13				16-17			
J		4						

Degradation Mode

A. Film Dissolution
B. Cyclic Changes (Charge Capacity and Optical)
C. Cyclic Changes (emf and Ion Trapping)
D. Mechanical (Hydrogen Embrittlement)
E. Transparent Conductor Etching
F. Gas Generation
G. Humidity Dependence
H. Secondary Chemical Reactions
I. UV Photochromism
J. Thermal Dependence and Decomposition

Load Type

1. Cyclic Volt./Current
2. Temperature
3. Humidity
4. UV Radiation
5. Outdoor Exposure
6. Weather-O-Meter
7. Static Conditions
8. Internal Water

5. Acknowledgments

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3. STABILITY AND AGING OF SELECTIVE ABSORBER COATINGS

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1. Introduction

The properties that characterize spectrally selective solar absorber coatings are absorptance for solar radiation and emittance for thermal radiation. Also, reliable adhesion and mechanical characteristics of the coatings and the collector substrate is important to the lifetime of the coating and the efficiency of the system.

These properties must fulfill the performance requirements for the specific application of the coating (see IEA Task X Subtask A) during the expected lifetime of the collector. Also in this way, the allowable degradation of the absorber can be defined.

Degradation is caused by loads (degradation factors), which accelerate or set up degradation processes (degradation modes) which change the composition of the absorber and its properties. Failure modes and their effect on performance can be determined by controlled qualification tests as functions of the load and the aging time.

2. Degradation Factors

The natural load of the absorber is composed of various degradation factors qualitatively and quantitatively depending on the collector type, the system design and the local climate.

Unavoidable degradation factors for photothermal solar energy conversion are the absorber temperature, cyclic temperature variation and the solar irradiation (mainly the ultraviolet). The degradation factors in non-evacuated collectors due to the energy and mass input from the surrounding atmosphere can change the absorber composition. Oxygen, humidity, moisture and pollutants like salt, sulphur dioxide and nitrogen oxides are also considered as degradation factors.

The effects of the single degradation factors are normally studied in accelerated indoor aging tests. Separate factors are studied in order to identify specific susceptibilities of the absorber. But synergetic effects may occur with combined loads. Real combined loads are difficult to simulate in accelerated laboratory tests. Outdoor tests provide the real test condition but are uncontrolled and unreproducible. Testing under natural conditions is usually done at in-use conditions. Correlations between real testing and controlled laboratory testing are very difficult to make.

The twelve degradation factors for absorbers are used in the matrix reporting formats. They are numbered as follows:

1. Constant temperature in air (or reactive gas)
2. Constant temperature in vacuum (or inert gas)
3. Cyclic temperature in air (or reactive gas)
4. Cyclic temperature in vacuum (or inert gas)
5. Radiation (solar or simulated solar) in air
6. Radiation in vacuum (or inert gas)
7. Humidity
8. Condensation
9. Water bath or water spray
10. Pollutants
11. Combined indoor tests (e.g., humidity and radiation)
12. Outdoor stagnation tests

3. Degradation

3.1. Optical properties degradation

The degradation modes change the physical and/or chemical composition of the absorber coatings. Because of this the refractive index, the optical thickness or the surface morphology are changed and might influence the spectral absorptance and reflectance in the solar and infrared spectral range (about 0.2-40μm). This will result in a change of the optical performance.

The sensitivity of the optical properties of the coating to the degradation modes depends on the type of spectral selectivity (tandem stack, interference stack etc.). These types have been discussed in detail by A.B. Meinel and M.P. Meinel (Applied Solar Energy, Wesley, 1976) as well as W.F. Bogaerts and C.M. Lampert [Materials for Photothermal Solar Energy Conversion, J. Mat. Science, 18, (1983) 2847-2875].

3.2. Decomposition

Another failure mode that reduces heat-transfer to the fluid, is the decomposition of the absorber layer due to blistering or peeling off from the substrate. The degree of blistering or peeling is determined according to standardized test procedures.

3.3. Outgassing

Impurities or volatile reaction products outgassing from the absorber may condense on the glazing which in turn decreases the transmission, or deteriorate the vacuum in evacuated collectors. The vacuum level or partial pressure of the emitted substances must be measured during the ageing.

4. Degradation Modes

The degradation modes leading to the failure can be classified as follows:

Energy Input:

1. Internal diffusion
   Intentional boundaries between layers may be destroyed by diffusion.
2. Internal chemical reaction
   Absorber materials can form new interfacial compounds, especially between different layers (e.g., metal/dielectric).
3. Morophological change
   After being deposited in a non-equilibrium condition the layer may tend towards an equilibrium, in terms of surface morphology or crystal structure.
4. Desorption
   Impurities incorporated during the deposition can leave the layer by desorption to the atmosphere.
5. Mechanical degradation
   Differences in the thermal expansion of absorber and substrate may cause blistering or microcracks.

6. Photodegradation
The solar irradiation (especially the UV-portion) may accelerate other degradation modes by photocatalysis or initiate new ones.

Mass Input:

7. External diffusion
The movement of chemical species from the environment into the coating. Often it occurs in combination with chemical reactions in the depth of the coating (e.g., oxidation of the substrate).

8. External chemical reaction
Components of the surrounding atmosphere act as reaction partner at the surface (mainly oxidation).

5. Analytical Methods

Numerous methods for surface analysis (Auger, ESCA, SIMS, etc.) have been developed (see e.g., A.W. Czanderna, "Surface and interface studies and the stability of solid solar energy materials", in Solar Materials Science, ed. L.E. Murr, Academic Press, New York, 1980, 93-147), for the investigation of the degradation modes described above. However, these techniques tend to be expensive.

- Measurement of UV-VIS-IR spectral reflectance (0.2-40μm)

These measurements have often already been carried out for the determination of the absorber performance and its degradation. But moreover, information can be obtained about the band gap of semiconductors, the optical path in interference stacks, molecular absorption bands and about the surface morphology by comparison of the hemispherical and the specular reflectance.

- Scanning electron microscopy (SEM) and transmission electron microscopy (TEM)

The surface morphology as well as microcracks and blistering can be investigated with SEM. The internal structure, composition and crystal phase can be investigated with TEM.

- Sputter-Auger-electron analysis (AES)

Chemical information with depth can be obtained by combined ion-beam sputtering and Auger spectroscopy. Degradation modes like diffusion and external chemical reactions can be detected by using sputter AES. AES is most sensitive to the lighter elements.

- X-ray photoelectron spectroscopy for chemical analysis (ESCA or XPS)

This method uses an X-ray probe to stimulate photoelectrons of the sample. This photoelectron spectra can be correlated to chemical binding energy. This is a surface technique useful for chemical compound identification.

- X-ray diffraction (XRD)

X-ray diffraction is used for the identification of crystal structures and chemical compounds without good depth resolution. XRD is most sensitive to the heavier elements.

- Secondary ion mass spectroscopy (SIMS)

SIMS is mass spectroscopy of the sputtered species during ion beam sputtering of a sample. It is highly sensitive and helpful for the detection of impurities and weak diffusion processes. It is the most reliable method for the investigation of adsorbed hydrogen and hydrogen compounds.

- Gas analysis

Outgassing by aging in vacuum can be observed with small mass spectrometers.

6. Selected Selective Solar Absorbers

The durability of numerous absorber coatings has been investigated in many research works. In the following, only parts of the published reports are taken into account. This study is only concerned with the materials selected by the participants of IEA Task.

The selected materials are classified as follows:

A Black chrome on stainless steel

B Black chrome on nickel

C Black chrome on other substrate materials

D Cermets produced by physical vapour deposition

E Cermets produced by sputtering

F Cermets produced by reactive processes

G Black zinc selective absorber surfaces

H Selective paints

I Nickel-pigmented anodized aluminum

J	Black Nickel
K	Blue stainless steels
L	Black cobalt

Portions in the following chapters are devoted to selected materials, G, H and I.

7. Conclusions

The results of literature studies for black chrome and other composite selective absorbers (cermet) are compiled in the following matrices. This overview only samples some of the work published (~38 papers). However, the total number of 85 different material/load combinations reported in these papers allows a good view of the preferred materials and loads as well as of the missing investigations (see Material/Load-Matrix 1).

The most favored material is black chrome on nickel. It was also the only material tested using irradiation, humidity or outdoor stagnation conditions. Usually, constant temperature tests were carried out, many in air, and some in vacuum (mainly for cermets in category F, used in evacuated tubes). There are no analyses with the degradation of black chrome under condensation, with the influence of pollutants and under normal operating conditions. The effects of radiation and temperature cycles should be investigated more in detail. Other cermet materials are more designed for evacuated collectors. Therefore only further investigations of the degradation by radiation, cyclic temperatures, or outdoor exposures are needed for them. For the materials listed as H, J, K and L there are no Degradation Mode/Load Matrices.

In most of the reports the degradation only is described qualitatively without taking into account the dependence of the load and the time, quantitatively. Also, the degradation modes often are not clearly identified. Some of the investigations were only carried out by the laboratory developing the absorber and therefore the results cannot be verified by comparison with others. But on the other hand, the results of several authors, investigating the same material, often are contradictory.

Thus more detailed literature studies in some cases as well as further research work, especially with regard to the quantitative correlation of failure mode, degradation mode and degradation factors, seem to be necessary.

7.1. Dominate Failure and Degradation Modes

A. Black chrome on stainless steel

Low interest, but high stability. Only heating in air was used. One study reports a weak cyclic temperature test, which is insufficiently described. Optical properties degradation caused by oxidation of the chromium or the substrate surface was found.

B. Black chrome on nickel

In all cases, the degradation of the optical properties was investigated. Decomposition of the absorber was caused by humidity (95% at 90 °C) in two cases. At low temperature loads (indoors as well as outdoors) one author supposed the reduction from Cr^{6+} to Cr^{3+}. At high temperatures oxidation of metallic chromium was found to be the main degradation mode together with changes in the surface structure.

C. Black chrome on other substrate materials

Of the few reports found, they mainly find problems with substrate diffusion and substrate oxidation at constant temperature loads.

D. Cermets produced by PVD

Cermets consisting of noble-metals in a dielectric are very stable at high temperature loads even in air. Cermets are recommended for high temperature collectors.

E. Cermets produced by sputtering

Good thermal stability of the cermets even in air is reported. Copper substrates (used as IR-reflectors) degrade in air.

F. Cermets produced by reactive processes

All the reviewed publications come from the same laboratory (University of Sydney, Australia). The main problem is the deterioration of the vacuum by outgassing of impurities in the absorber, which were incorporated during the deposition process.

G. Black zinc selective absorber surfaces

Black zinc coatings of ZnO may be formed by the anodic oxidation of leaf-zinc. Black zinc coatings are found to be zinc rich oxides with a surface microroughness of the order of solar wavelength dimensions. Optical properties are good. Values of α as high as 0.98 are reported and many surfaces with α >0.95 have been produced. Thermal emittance, ϵ, values generally lie in the range 0.10-0.20. The surfaces have also been formed on steel substrates and in these surfaces typical values of ϵ are 0.25. Optical properties are strongly dependent on deposition process conditions.

Optical properties have been successfully modelled using effective medium theories and this approach has been extended to the assessment of surface change following durability testing [A. Scherer and O.T. Inal, Applied Optics (20), 3348, 1985].

Degradation mechanisms have been variously interpreted. Some papers report oxidation of excess zinc while others report changes observed following exposure to high temperatures as being due to growth of zinc and changes in particle size. The high temperature stability of zinc oxide on steel is questionable because of the formation of Zn-Fe compounds at the film substrate interface.

Black ZnO films can also be produced by reactive bias rf sputtering [M.J. Brett, R.R. Parsons and H.P. Baltes, Applied Optics (16), 2712, 1986]. The bias conditions can be altered to produced transparent electrically conducting heat mirrors. An initial report of a black zinc oxide film overlaid with a transparent ZnO heat mirror is of significant interest although no durability tests have yet been reported. An advantage of the sputtered coating is its ease of application to glass substrates and hence its potential for use in evacuated tubular collectors.

H. Selective Paints

Serious research has been conducted in the United States, particularly by the Honeywell Research Centre, which has resulted in the development of selective paints whose optical response is most encouraging. However, this work would appear to be at an end due to lack of further funding. To date research has concentrated on materials using either Silicon or Urethane binders, and paints which are either thickness sensitive or thickness insensitive. Honeywell has produced a thickness sensitive, Silicone binder paint with a $\alpha = 0.92$ and $\epsilon = 0.14$ as prepared. Durability of thickness sensitive paints using Silicone binders is reported as favorable. Thickness insensitive paints using Urethane binders are reported as being unsuitable for active solar use.

Only a limited number of publications have appeared describing selective paints and of these none have evaluated degradation modes. Adhesion tests carried out on one paint revealed favorable adhesion qualities.

I. Nickel Pigmented Anodized Aluminum

Nickel pigmented aluminum oxide thin film coatings have been developed for the selective absorption of solar radiation. Porous aluminum oxide is formed by dc anodization in dilute phosphoric acid. Nickel particles are incorporated into the Al_2O_3 film by ac electrolysis in a $NiSO_4$ bath. Metal content can be adjusted through variation of the deposition process parameters [A. Anderson, O. Hunderi and C.G. Granqvist, J.Appl.Phys. 51 (1), 754, 1980.

The structure of nickel particles embedded within the pores of the oxide matrix has been confirmed by a range of surface analytical techniques which include SEM, AES, and XPS studies.

The optical properties of prepared coatings are strongly dependent on the deposition process conditions. Optimum values of solar absorptance, α, and thermal emittance, ϵ, are generally reported to be $\alpha = 0.95$, $\epsilon = 0.15$.

The coating was first produced commercially in Sweden under the trade name Sunstrip. This product is now marketed by Sunstrip International Inc., Canada. A similar coating, produced in Japan, was used as the absorber surface for the Sanyo evacuated tubular solar collector.

Only a limited nubmer of publications have appeared described development work on this coating. In all cases durability has been reported to be good with little or no degradation of surface optical properties being observed following exposure to controlled thermal cycling in the presence of moisture or exposure at elevated temperatures in air.

Effective medium models have been successfully applied to the coating structure to predict surface optical repsonse.

Recent studies [N.M. Nahar, G.H. Mo and A. Ignatiev, Solar Energy Materials 14, 129, 1986] have shown that the deposition process may be simply adapted to the production of cobalt pigmented aluminum oxide selective absorbers [N.M. Nahar, G.H. Mo and A. Ignatiev, Solar Energy Materials 14, 129, 1986]. This surface is reported to have superior reflectance curve of Co in Al_2O_3 following exposure at high temperatures, which indicates a loss in optical thickness, is attributed to oxidation and some dispersion of the cobalt in the oxide overlayer. No significant optical change has been observed in a study of the thermal stability of NiinAl_2O_3 [M.G. Hutchins, P.R. Dolley and G.W. Lloyd, Proc IEA SHAC Task X Workshop, Tokyo, Japan, May 1987.

J. Black Nickel

All the reported data was on the Maxorb type of black nickel. this coating is stable to 300 ° C) including different humidity conditions. One of the failure modes was degradation of the adhesive which caused wrinkling of the absorber surface. Additional detail about the stability of the adhesive can be found in C.M. Lampert, Plating and Surface Finishing 20 (1980) 52.

K. Blue Stainless Steel

A range of blue stainless steels were studied. Generally these coatings are stable with temperature, but they do exhibit some unexplained emittance increase. The degradation modes are not identified.

L. Black Cobalt

The stability of black cobalt on copper was studied. It was found to be stable up to 400 ° C) but subject to surface oxidation. The dominate degradation mechanism was oxidation of the copper substrate.

Failure and Degradation
Material/Load-Matrix
Selective Solar Absorbers

Number of reviewed publications: 38

	Load											
Materials	1	2	3	4	5	6	7	8	9	10	11	12
A	3		1									
B	15	1			2	1	4					4
C	4		1									
D	5											
E	2	2										
F		6										
G	5				1							
H							2				5	1
I	4		1		2		3					
J	2						2					
K	2						2					
L	2											

Failure and Degradation Mode/Load-Matrix
Material: A (Black chrome on stainless steel)

	Load											
FAILURE MODE	1	2	3	4	5	6	7	8	9	10	11	12
Optical property degradation	1,2 3		1									
Decomposition												
Outgassing												
DEGRADATION MODE	1	2	3	4	5	6	7	8	9	10	11	12
Int. diffusion												
Internal chemical reactions												
Morphological changes												
Desorption												
Mechanical degradation												
Photo degradation												
Ext. diffusion	3											
Ext. chemical reactions	1,2 3											

Failure and Degradation Mode/Load-Matrix
Material: B (Black chrome on nickel)

Load												
FAILURE MODE	1	2	3	4	5	6	7	8	9	10	11	12
Optical property degradation	1-15	1			1,2		1-4					1-4
Decomposition							1,4					
Outgassing												
DEGRADATION MODES	1	2	3	4	5	6	7	8	9	10	11	12
Int. diffusion	12,14				1							
Internal chemical reactions	1,8-10 13,14	1										
Morphological changes	1,2 4,5 8-10	1					4					
Desorption	13	1			1,2	1						
Mechanical degradation							1,4					
Photo degradation												
Ext. diffusion	11,14						1					
Ext. chemical reactions	3-7 9,11-14				2		1-4					2

Failure and Degradation Mode/Load-Matrix
Material: C (Black chrome on other substrate materials)

	Load											
FAILURE MODE	1	2	3	4	5	6	7	8	9	10	11	12
Optical property degradation	1-4											
Decomposition												
Outgassing												
DEGRADATION MODE	1	2	3	4	5	6	7	8	9	10	11	12
Int. diffusion	1,2,4											
Internal chemical reactions												
Morphological changes	3											
Desorption												
Mechanical degradation												
Photo degradation												
Ext. diffusion												
Ext. chemical reactions	1,2 4											

Failure and Degradation Mode/Load-Matrix
Material: D (Cermets produced by PVD)

	Load											
FAILURE MODE	1	2	3	4	5	6	7	8	9	10	11	12
Optical property degradation	1-5											
Decomposition	1,2											
Outgassing												
DEGRADATION MODE												
Int. diffusion	5											
Internal chemical reactions												
Morphological changes												
Desorption												
Mechanical degradation												
Photo degradation												
Ext. diffusion	3,5											
Ext. chemical reactions	3,5											

Failure and Degradation Mode/Load-Matrix
Material: E (Cermets produced by sputtering)

	Load											
FAILURE MODE	1	2	3	4	5	6	7	8	9	10	11	12
Optical property degradation	2	1										
Decomposition	1,2	2										
Outgassing												
DEGRADATION MODE	1	2	3	4	5	6	7	8	9	10	11	12
Int. diffusion	2	1,2										
Internal chemical reactions		1										
Morphological changes	1	1										
Desorption												
Mechanical degradation	1											
Photo degradation												
Ext. diffusion	1,2											
Ext. chemical reactions	1,2											

Failure and Degradation Mode/Load-Matrix
Material: F (Cermets produced by reactive process)

	Load											
FAILURE MODE	1	2	3	4	5	6	7	8	9	10	11	12
Optical property degradation		1,4-6										
Decomposition	1,2	2										
Outgassing		1-4 6										
DEGRADATION MODE	1	2	3	4	5	6	7	8	9	10	11	12
Int. diffusion		5										
Internal chemical reactions		6										
Morphological changes		4										
Desorption		1-4										
Mechanical degradation		1,4										
Photo degradation												
Ext. diffusion												
Ext. chemical reactions												

Failure and Degradation Mode/Load-Matrix
Material: G (Black zinc)

	Load											
FAILURE MODE	1	2	3	4	5	6	7	8	9	10	11	12
Optical property degradation	1-3, 5											
Decomposition												
Outgassing												
DEGRADATION MODE	1	2	3	4	5	6	7	8	9	10	11	12
Int. diffusion												
Internal chemical reactions	1-3, 5											
Morphological changes	1,2 5											
Desorption												
Mechanical degradation	5											
Photo degradation												
Ext. diffusion												
Ext. chemical reactions												

Degradation Mode/Load-Matrix

Number: Ref. Date: May 1987

Materials Category: I (Ni in Al_2O_3)

	Load											
Material mode	1	2	3	4	5	6	7	8	9	10	11	12
Optical properties degradation	3,4				1,2		2					
Decomposition												
Outgassing												
Degradation mode												
Int. diffusion					1,2							
Internal chemical reactions					1,2							
Morphological changes							2					
Desorption												

4. THERMAL STORAGE MEDIA

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1. Introduction

Issues concerning stability and degradation of five material categories (Sodium sulfate decahydrate, Calcium chloride hexahydrate, Pentaerythritol, high density Polyethylene and Paraffin) were surveyed. We have examined nineteen documents which are represented in thirteen Reference Reporting Sheets. As for paraffin, no documents regarding degradation could be found. Most of the investigations for paraffin were related to the improvement of its heat transfer performance. This may indicate that there are few phase change stability problems for paraffin.

As is shown in the Material/Load-Matrix (Table 1), the most common degradation load for thermal storage materials is cyclic temperature. We could find only a few works examining the effects of other loads.

Durability under melting-freezing conditions is the most fundamental performance criterion for phase change heat storage materials, so the degradation test with cyclic temperature is thought to be the most important test method, and the principal degradation mode may be investigated by this test. As the latent heat thermal storage materials are considered to be used almost always in closed vessels and not to be exposed to outdoor conditions, the degradation loads would be considerably limited. Therefore, there is no substantial need for testing in the twelve degradation load categories in Matricies.

1.1. Summary of the Survey

1.2. $Na_2SO_4 \cdot 10H_2O$

The degradation mode of pure $Na_2SO_4 \cdot 10H_2O$ (Glauber's salt) as a thermal storage material during the melting-freezing cycle is identified as incongruent melting (Table 2).

Pure Glauber's salt melts incongruently because anhydrous Na_2SO_4 is insoluble in the water of crystallization released during the melting. Consequently, when Glauber's salt

Table 1.

Material/Load-Matrix

Number:

Materials Category: Thermal Storage Media

Total number of considered reference reporting sheets: 13

Number of reviewed publications: 19

Materials	Load											
	1	2	3	4	5	6	7	8	9	10	11	12
A		8										
B		3										
C	1	1										
D		1										
E		0										

Materials

A: $Na_2SO_4 \cdot IOH_2O$
B: $CaCl_2 \cdot 6H_2O$
C: Pentaerythritol
D: High Density Polyethylene
E: Paraffins

Loads

1. constant temperature
2. cyclic temperature
3. humidity
4. condensation/water spray
5. water bath

6. pollutants
7. normal radiation
8. combined indoor tests
9. outdoor stagnation
10. outdoor service conditions
11. accelerated test conditions
12. concentrated radiation

Table 2.

Degradation Mode/Load-Matrix

Corresponding Material/Load Matrix: A
Material: Sodium sulfate decahydrate

Degradation mode	1	2	3	4	5	6	7	8	9	10	11	12
Diffusion												
External chemical reactions												
Internal chemical reactions												
Phase transformation												
Crystallization		1,2,3, 4,5,6, 7,8										
Outgassing												
Mechanical degradation												
Photo degradation												
Decomposition												
Optical property degradation							1,4					

melts, about 15 per cent of the solid Glauber's salt precipitates as anhydrous Na_2SO_4 which, being more dense than the solution, settles to the bottom of the container. Thus, phase separation occurs.

Also, crystals of Na_2SO_4 gradually grow during melting-freezing cycles. When the phase separation or the growth of the crystals of Na_2SO_4 occurs, hydration reaction in the recrystallization process reduces its reaction rate or becomes incomplete. Consequently the retrievable heat is decreased and heat storage performance deteriorates.

Pure Glauber's salt exhibits severe supercooling like other salt hydrates and spontaneously nucleates the undesired heptahydrate phase. The addition of $Na_2B_4O_7 \cdot 10H_2O$ (borax) as a nucleating agent has solved both problems satisfactorily.

To solve the problem of deterioration caused by the phase separation, rotating a container of the salt to minimize gravity effects or mixing with appropriate thickening agents to homogenize the melting salt has been investigated, as is shown in Reference Reporting Sheets.

1.3. $CaCl_2 \cdot 6H_2O$

Pure calcium chloride hexahydrate exhibits supercooling and phase separation in the melting-freezing cycle that causes the degradation of heat storage performance (Table 3). Supercooling is considered to be fundamentally related to the interaction between water molecules and ions of the molten hydrate.

Phase separation is caused by the formation of $CaCl_2 \cdot 4H_2O$ during repeated freeze-thaw cycling. If $CaCl_2 \cdot 4H_2O$ is formed, it causes stratification, yielding $CaCl_2 \cdot 4H_2O$, $CaCl_2 \cdot 6H_2O$ and a saturated aqueous solution of $CaCl_2 \cdot 4H_2O$ and the saturated solution with repeated phase change.

Supercooling can be overcome by using a barium salt such as $BaOH_2 \cdot 8H_2O$ or BaF as an effective nucleating agent.

To suppress phase separation, addition of such an agent as excess water, or sodium chloride is proposed. (Reference Reporting Sheet No. 10).

Table 3.

Degradation Mode/Load-Matrix

Corresponding Material/Load Matrix: B Date:
Material: Calcium chloride hexahydrate

Degradation mode	1	2	3	4	5	6	7	8	9	10	11	12
Diffusion												
External chemical reactions												
Internal chemical reactions												
Phase transformation												
Crystallization		8,9, 10										
Outgassing												
Mechanical degradation												
Photo-degradation												
Decomposition												
Optical property degradation												

1.4. Pentaerythritol

The deterioration of pentaerythritol was investigated over two months of a heating-cooling cycle: 8-hour holding at 200° C as the highest temperature in a day followed by 5-hour holding at 30° C as the lowest. Several changes in pentaerythritol by the heating-cooling cycles, e.g., weight decrease, decrease in oxygen content, production of a carbonyl compound, and lowering of the heat of transition and of the transition temperature, are thought to be caused by sublimation, thermal oxidative decomposition, and crosslinking between produced radicals (Table 4). Radical scavengers effectively suppressed the thermal degradation of pentaerythritol. To use pentaerythritol as thermal storage material, the suppression of sublimation, of oxidation and of radical production is required (Reference Reporting Sheet No. 11).

The compatibility with some heat transfer fluids, which were used in direct contact with pentaerythritol as a slurry, was also examined by keeping them in an energy-stored state and then observing the heat of transition by Differential Scanning Calorimetry. Hydrocarbon as a heat transfer fluid was found to be suitable (Reference Reporting Sheet No. 12).

1.5. High Density Polyethylene

The deterioration of high density polyethylene was investigated by applying the heating-cooling cycle which simulates daily insulation over six months (8-hour holding at 150° C as the highest temperature in a day followed by 5-hour holding at 30° C as the lowest.)

The result of degradation is the lowering of heat of crystallization and that of crystallization temperature, and is thought to be caused by both the decrease in molecular weight of polyethylene due to thermal oxidative decomposition and by the crosslinking between produced radicals (Table 5). With the increase in the degree of crosslinking and branching which has low bond disassociation energy, thermal deterioration of polyethylene proceeds more rapidly. Polyethylene pellets can endure long periods of practical heat cycling as a thermal storage material when they are treated with radical scavengers under proper control of their degrees of crosslinking (Reference Reporting Sheet No. 13).

Table 4.

Degradation Mode/Load-Matrix

Corresponding Material/Load Matrix: C
Material: Pentaerythritol

Load												
Degradation mode	1	2	3	4	5	6	7	8	9	10	11	12
Diffusion												
External chemical reactions												
Internal chemical reactions												
Phase transformation		11										
Crystallization												
Outgassing												
Mechanical degradation							2,3, 5					
Photo degradation												
Decomposition		11										
Optical property degradation							1,4					
Crosslinking		11										

Table 5.

Degradation Mode/Load-Matrix

Corresponding Material/Load Matrix: D
Material: High-density polyethylene

Load												
Degradation mode	1	2	3	4	5	6	7	8	9	10	11	12
Diffusion												
External chemical reactions												
Internal chemical reactions												
Phase transformation												
Crystallization												
Outgassing												
Mechanical degradation												
Photo degradation												
Decomposition		13										
Optical property degradation												
Crosslinking		13										

1.6. Paraffins

Paraffins are mineral oil products mostly of the Alkanes family C_nH_{2n+2}. The paraffins have promising characteristics including chemical stability. The drawbacks are lower volumetric energy density than the salt hydrates, 10% volume change upon phase change, and poor thermal conductivity.

2. Conclusions

The greater part of investigations about phase change heat storage materials is related to durability and stability for repeated melt-freeze cycling, which is thought to be the most fundamental performance for the materials. This means that most of the phase change heat storage materials do not have sufficient stability for repeated phase change, which is necessary in practical use.

For the phase change heat storage materials as described above, there would not exist especially important degradation loads except for the cyclic temperature. If there is a case for the materials to be used in outdoor conditions, research on degradation with the loads such as radiation, pollutants and so on would be necessary. But there would scarcely be such a case in those conditions.

Therefore, durability for cyclic temperature is thought to be the most important performance for the phase change heat storage materials also in the future. From this viewpoint, it is necessary to investigate durability when additives such as nucleating agents, thickeners and so on are included. For practical use, it is important to know the limit of temperature stability and to know the stability in the presence of the container, encapsulant and heat transfer medium used with each material.

Therefore, the following future cooperative works are proposed:

(1) Durability of the phase change materials under a cyclic temperature and identification of degradation modes.

(2) Confirmation of the limit temperature to be used for each material and of the failure mode in each case.

(3) Investigation of co-existency for each storage material with containers, encapsulant and heat transfer media.

5. CONCLUSIONS

Carl M. Lampert

1. Collector and Window Glazings

Although there are a wide range of polymer glazings used in solar applications, only one polymer (PET) is discussed in this study. Low-emittance coated PET is used in many architectural window applications. Polymers in general are used in a variety of glazings but many limited in their lifetime by UV and combined exposures. Polymers have a very important future for glazings and should be improved for solar applications. Polymers offer light weight, ease of fabrication and low cost compared with most other materials. The study of the cementation and dusting of glazings is important to the overall performance of the glazing and system. Also, not covered by this study, but very important is the stability of polymers used as substrates or superstrates for reflectors.

2. Glasses

Glass is a very stable material for glazings, its two drawbacks are weight and poor resistance to physical impact. A wide range of data was found on low-iron tempered float glass. It has been tested under 10 different loads, the most tested of any material. The three modes of degradation were found to be weathering, stress corrosion/strength reduction and solarization. Studies on the stability of wavelength selective coatings and antireflection treatments on glass are needed.

3. Polyethylene Terephthalate (PET)

The major degradation mode of PET is photodegradation which results in both mechanical and optical property changes. A study on the long term stability of low-emittance coated PET used in windows is needed. For PET a good correlation is needed to compare accelerated weathering to outdoor real time service conditions.

4. Sealants

Sealants appear to be the weakest part of collector and window glazings. Glass sealants degrade under a combination of stresses, including solar radiation, moisture, heat and mechanical stressing. The usual failure mode of a sealed glass unit is the deposition of contaminants or moisture on the inner surfaces of the glazing which impairs optical transmittance and clarity. Gas and moisture permeation though seals can lead to degradation of internal components of the collector or window and is particularly hard on wavelength selective coatings. There is need to characterize the internal conditions "micro-climate" of both collectors and window glazings. The degradation modes are not well understood and should be studied in more detail for a variety of windows and sealant configurations.

5. Electrochromic Optical Switching Films

This is a developing area for window glazings. Because these materials are new fairly little is known about their stability. Some aspects of lifetime are determined by how the films are used and operated. Several effects control the stability of prototype electrochromic films including cyclic potential, thermal dependence and photoreactions. A variety of problems are noted, some can be solved by better design and understanding of the degradation mechanisms. Characterization parameters and test methods need to be standardized. The dominate modes of aging need to be determined. No correlations exist between laboratory testing and outdoor exposure.

6. Selective Absorbers

Generally selective surfaces are tested in controlled laboratory environments, in direct or glazed outdoor exposure or in actual collectors, operating or stagnating. In the laboratory, selective absorbers are usually tested under constant temperature (in air or vacuum). Some information about humidity effects are known, too. The effects of other stresses are generally unknown. The nature of the internal collector environment "micro-climate" needs to be characterized. The effect of radiation and temperature cycling should be better understood. For most absorbers, degradation modes are not well identified or disputed. The most information is known about black chrome on nickel. Black chrome degrades at elevated temperatures, generally above 400°C. It degrades by oxidation of the metallic phase and densification of the coating. Better correlation is needed between laboratory and outdoor degradation testing of solar absorbers.

A few of the newer selective absorbers are selective paints, nickel pigmented anodized aluminum and black zinc. All of these absorbers require further study. Selective paints are a very important absorber type because of their potential to reduce the cost of selective absorber coatings by a factor of 10 and increase their versatility. The stability and degradation modes of paints are largely unidentified at this time. The coatings are still in the research stage. Silicone binder based selective paint appears to be more stable compared to the urethane type. Very little is published about Nickel Pigmented Anodized Aluminum. From what is known it appears to be a fairly stable coating under thermal cycling and moisture. The Black Zinc Selective Absorber is a fairly new selective coating for steel, its degradation properties are not well investigated. There is concern about Zinc oxidation the formation of Zinc-Iron compounds at elevated temperatures.

7. Thermal Storage Media

Five thermal storage materials were investigated. They are sodium sulfate decahydrate, calcium chloride hexahydrate, pentaerythritol, high density polyethylene and paraffin. Since thermal storage materials are generally in closed systems they are not generally sensitive to the large range of exposure stresses seen in other solar materials. The most common failure stress is cyclic temperature. The salts exhibit failure due to phase separation. Various additives are used to control this problem. Pentaerythritol is thought to exhibit degradation by sublimation, thermal oxidative decomposition and crosslinking. High density polyethylene exhibits similar degradation problems as in pentaerythritol, but without sublimation. It is generally accepted that paraffins are stable and very useful for thermal storage. Very little information was found on the degradation of paraffins. The result of this work suggests that further studies be done on thermal storage materials concerning failure mode identification, and temperature limits. Also, a better understanding of the interaction of the storage material and containers, encapsulants and heat transfer media is suggested.

APPENDIX A

STABILITY AND DURABILITY OF ELECTROCHROMIC SWITCHING FILMS FOR GLAZINGS

APPENDIX A

Stability and Durability of Electrochromic Switching Films for Glazings

On the following pages are reference reporting sheets that detail the findings of specific references. Only the references that have additional information of direct interest to this study are included on these sheets.

REFERENCE REPORTING SHEET

ID-Code: D-1 **Number:** 4

Reporters Name: C. M. Lampert **Ref. Date:**1986

Coating/Substrate: Glass/SnO_2/a-WO_3/$LiClO_4$-PC/ Prussian Blue /SnO_2 /Glass. Also a third electrode of poly-4,4',4"-triphenylamine is used to electrochemically stabilize the cell.

Manufacturer: Nissan Motors, Yukosuka, Japan

Load: Temperature, Cyclic Voltage , UV irradiation

Test Procedure: The device was 37cm x 37cm in size.

(1) Accelerated cyclic durability test. The device driving potential was a cyclic D.C square-wave potential of +1.0V for coloration and -0.5V for bleaching. The period for coloration was 20 s and for bleaching was 40 s.

(2) For the study of electrolyte decomposition temperature testing was performed from 32-100 C for 0-80,000 hrs. Also, thermal performance of a-WO_3 was studied.

(3) UV irradiation at 63 C for 1050 hrs. The change in injected charge for a fixed coloration/bleach cycle was measured.

(4) Long term memory test. Study of the change in optical density with time under no applied voltage.

Optical Properties (Before and After Testing):

(1) Initial experiments showed T_v(bleached)= 0.60, T_v(colored)=0.08. After a few thousand cycles, T_v(bleached)=0.60 and T_v(colored)=0.15. After addition of 1-2% water to the electrolyte, T_v(colored)=0.08 after 8,000 cycles.

(2) The decomposition of the electrolyte occured after 10^3 hrs. at 60 C and $3x10^2$ hrs. at 70 C and $2x10^2$ hrs. at 80 C and 15 hrs. at 90 C.

(3) Injected charge dropped from 13 to 8 mC/cm^2 after 1000 hrs. of UV irradiation in a Weather-O-Meter at 63 C.

(4) No optical change after 7 days, T_v(bleached)=0.52 and T_v(colored)=0.08.

Analytical Methods:

(1,3)Cyclic voltammetry , (1-4) spectrophotometry, (2) X-ray Photoelectron Spectroscopy (XPS)

Degradation or Failure Modes:

(1) Shift in voltammetry peaks and decrease in charge injection level. It appears that the prussian blue layer requires some water to switch properly.

(2) Chemical decomposition, showing chemical shifts in XPS spectra, Also, change in WO_3 spectra, suspect that: $W\text{-}O\text{-}H + Li^+ \text{-->} W\text{-}O\text{-}Li + H^+$ with temperature.

(3) Photo induced effect, WO_3 is photosensitive, the mechanism is unidentified.

Comments:

It was determined that the safe operating range for the device was 0.8 to 1.4V for coloration and -0.5 to -1.5V for bleaching. The coloration response time was 3 min (at 1.0V) and the bleaching response time was 2 min (at -0.5V) for a 40x40 cm device. The films were deposited by a combination of electrodeposition and vacuum evaporation (100 C). Much of this data is preliminary and it is expected that further work will be published in the future.

Reference:

T. Kase, M. Kawai and M. Ura, " A New Electrochromic Device for Automotive Glass-The Development of Adjustable Transparency Glass" Proc. SAE Meeting, Sept 22-25, 1986. and personal communications with Nissan Motors.

REFERENCE REPORTING SHEET

ID-Code: E-1
Number: 5
Ref. Date:1987
Reporters Name: C. M. Lampert
Coating/Substrate:glass/ITO/a-WO_3/Poly-AMPS/a-IrO_2/ITO/glass.
Manufacturer: EIC Labs, Norwood, MA ,USA
Load: Cyclic switching

Test Procedure:
Cycled with a potentiostat using a voltage of -0.2 for bleaching to 1.0 V for coloration, at 200mV/s.

Optical Properties (Before and After Testing):
After the first cycle the injected charge level was 15.2 mC/cm^2 the absorptance change ΔA=0.31 with a maximun transmittance of 0.74 at 530 nm. after $2.1x10^4$ cycles the charge transfer dropped to 7.9 mC/cm^2,ΔA= 0.18 and the transmittance was 50.1 at 530nm. After this the coloring potential was raised to 1.0V and the charge injection went to 10.6 mC/cm^2,ΔA=0.22 and the transmittance was 51.3. After 10^5cycles the charge level was 9.5 mC/cm^2 , ΔA= 0.24 and Transmittance of 51.3.

Analytical Methods:
Potentiostat, spectrophotometer

Degradation or Failure Modes:
Not identified, reduction in available protons for switching would effect the charge injection level.

Comments: This study also contains data on the effect of temperature (-20 to70 C) on charge transfer at various sweep rates. The speed of switching is reduced at lower temperatures.

Reference:
S.F. Cogan, T. D,. Plante, R.S. McFadden and R. D. Rauh, " Design and Optical Modulation of a-WO_3/a-IrO_2 Electrochromic Windows", Proc. SPIE 823(1987) in press.

REFERENCE REPORTING SHEET

ID-Code: F-1
Number:6
Reporters Name: C. M. Lampert
Ref. Date: 1982
Coating/Substrate:glass/SnO_2/a-WO_3/Poly-AMPS/C
Manufacturer: American Cyanamid, Stamford,CT, USA
Load: Cyclic current at 0.5 Hz, 22 C and 50 C.

Test Procedure:
Cyclic current +/- 350µA, Applied voltage limited to +/- 1.0V. The coloration and bleach cycles had 0.9 s intervals of applied power separated by a 0.1s rest interval between each half cycle.

Optical Properties (Before and After Testing):
0 to 60% contrast level was used for cyclic testing, the injected charge was 3.7 mC/cm^2. For reference a 50% and 70% contrast levels require 2.9 and 4.9 mC/cm^2 repectively.

Analytical Methods: Not cited

Degradation or Failure Modes:
No failure mode detected for $5x10^6$ cycles at 50 C and 10^7cycles at 22 C.
Moisture loss through the epoxy seals is responsible for breakdown at elevated temperatures.
Reduction of the SnO_2 is seen when driving potentials are above 1.0V.

Comments: This work was done on a non transparent display device. The results are important to the workers using Poly-AMPS as an ion-conductor in transparent devices.

Reference:
R.D. Giglia and G. Haacke," Performance Improvements in WO_2 based Electrochromic Displays", Proc. SID 23(1982)41.

REFERENCE REPORTING SHEET

ID-Code: G-1 **Number:** 9

Reporters Name: C. M. Lampert **Ref. Date:**1978

Coating/Substrate: SnO_2/WO_3/electrolyte/Pt, The WO_3 was evaporated.

Manufacturer: Ebauches SA, Neuchatel, Switzerland.

Load: Cyclic Potential at RT,50 C

Test Procedure:

(1)+/-2.5 mA/cm^2 for 1 s at 0.5 Hz with bleaching potential limited to1.35V

(2) Cyclic voltammetry from -0.9 to1.0V with Hg reference electrode.

Optical Properties (Before and After Testing): not given

Analytical Methods:

X-ray analysis, Differential thermal analysis for the study of reactions. Thermogravimetry for the study of weight loss during heating,SEM, potentiostat.

Degradation or Failure Modes:

The dissolution rate was 2-2.5 nm/day at 50 C and 1.8nm/day at RT for WO_3 in glycerine-H_2SO_4. The reaction is $WO_3 + 6h^+ \text{--->} W^{+6}$(solution)+ 3/2 O_2. The film crumbled after 30 days at 0.5Hz and CR=40%. This is caused by hydrogen embrittlement. The lifetime of the film was 42 days at 1.8×10^6 cycles. The WO_3 film is much more stable in aprotic electrolytes. Data is given for other electrolytes. A secondary mode of failure for the electrode might be electrochemical reduction of the SnO_2 layer following the reaction $SnO_2 \text{-->} Sn^{+4} + O_2 + 4e^-$.

Reference:

J. P. Randin, "Chemical and Electrochemical Stability of Electrochromic Films in Liquid Electrolytes" J. Electron. Mat. 7(1978) 47.

REFERENCE REPORTING SHEET

ID-Code: C-1 **Number:**13

Reporters Name: C. M. Lampert **Ref. Date:**1977

Coating/Substrate:$SnO_2/WO_3/LiClO_4$-PC/Li_xWO_3

Manufacturer: Zenith Radio corp., Research Dept., Glenview,Il

Load:(1) cyclic voltage (2) regenerated by UV light at 25, 40 C.

Test Procedure:

(1) Cyclic voltage using a square wave of +/-0.75V(vs. Pt) for 100 hrs. at 4 s per cycle.

(2) After 100 hrs and 9×10^4 cycles, voltage set to constant 1V bleaching and exposed to UV light.

Optical Properties (Before and After Testing):

(1) A contrast ratio of 4:1 was seen before cycling. The peak current density was 4 mA/cm^2 bleached and -5 mA/cm^2 colored. After 100hrs the peak current was 1 mA/cm^2 bleached and -4 mA/cm^2 colored.

(2) After UV regeneration the bleaching current became 2 mA/cm^2 and -5 mA/cm^2 colored.

Analytical Methods:

(2) 350 W Xenon lamp

Degradation or Failure Modes:

(1) During cycling a shift of -170 mV in the coloration potential was detected.

(2) The energy of the UV light was able to depopulate and eject trapped charge in the WO_3 film. The trapping states may be related to water in the film or photolysis of the electrolyte.

Reference:

T.J. Knowles,"Optical Regeneration of Aged WO_3 Electrochromic Cells"Appl. Phys. Lett. 31(1977)817.

REFERENCE REPORTING SHEET

ID-Code: A-1 **Number:** 14

Reporters Name: C. M. Lampert **Ref. Date:** 1986

Coating/Substrate: Glass/ITO/ a-WO_3/ $LiClO_4$+ Organic/Metal, produced by e-beam evaporation at RT

Manufacturer: Asahi Glass Co, Yokohama, Japan

Load: Cyclic Voltage at RT and 100 C.

Test Procedure:

(1) The electrode was tested in 1M $LiClO_4$ in butyloactone or propylene carbonate (PC). The water content was 0.1%. The electrodes were aged using a +1.25 to -1.25V square wave, 1Hz at RT and 100 C.

(2) Studied the role of water addition to the films. Diffusion of Li^+ is enhanced due to the addition of H^+ or water which lowers the activation energy for diffusion in the films.

Optical Properties (Before and After Testing): (1-2) no change noted

Analytical Methods:

Cyclic voltammetry, emf and small signal A.C. Impedance analysis, compositional analysis by X-ray fluorescence, AES and XPS. The amount of alkali determined by AA spectroscopy.

Degradation or Failure Modes:

(1) During cyclic coloration and bleaching (beyond 10,000 cycles), a decrease in injected charge is noted. The charge per unit area begins at 5-6 mC/cm^2 and drops to 4-1 mC/cm^2 at $5x10^5$ cycles. Only an electrochemical emf change is noted in the film.

After cycling, Li ions are found bound in the film structure and are not active in coloration but are responsible for the emf shift. With cycling the film in the bleached state becomes a more ion conductive as the result of Li incorporation. There appear to be two active sites for lithium ions:one for coloration; $WO_3 + xLi^+ + xe^- \leftrightarrow Li_xWO_3$ and another for ion exchange according to : $W\text{-}O\text{-}H + Li^+ \leftrightarrow W\text{-}O\text{-}Li + H^+$.

By application of the appropriate increased potential the film can be restored to its original switching properties.

(1) The O/W ratio increases during cycling. The WO_3 may form a metatungstate $(M^+)_6(W_{12}O_{39})$ where M = H, Li, etc., which can serve as an ion exchange site.

(2) A small amount of water in Li based systems enhances the films switching properties. However, too much water accelerates degradation of the film. More dense films are more stable than less dense ones.

Reference:

J. Nagai, T. Kamimori and M. Mizuhashi, "Electrochromism in Amorphous Lithium Tungsten Oxide Films", Solar Energy Materials,13 (1986) 279.

REFERENCE REPORTING SHEET

ID-Code: A-2, A-3 **Numbers:** 15,16

Reporters Name: C. M. Lampert **Ref. Dates:** 1984,1986

Coating/Substrate:glass/ITO/a-WO_3/$LiClO_4$+Redox/ITO/glass, produced by e-beam evaporation at RT

Manufacturer: Asahi Glass Co, Yokohama, Japan

Load: (1)Cyclic Voltage at RT and 100 C. (2) storage at different temperatures (3) cycling under indoor and outdoor conditions (4) accelerated simulated weathering.

Test Procedure:

(1) Color/bleaching cycles were carried out using a D.C. potential of 1.0V or -1.0V for a 3 min. interval. A 30x30 cm^2 device was used. Over 10^5 cycles were performed.

(2) Devices were cycled for 1 min. intervals under different temperatures of, RT, 50, 60, 90 C, for over 30 days. The device was 10x10 cm^2 in size.

(3) Color/bleaching cycles were done outdoors using a D.C. potential of 1.0V or-1.0V for a 1 min interval. Over 10^5 cycles were performed. A 10x10 cm^2 device was used.

(4) A device was cycled in a Weather-O-Meter at 60 C with an exposure to a carbon arc lamp for over 2000 hrs. Both 10x10cm^2 and 30x30 cm^2 devices were tested.

Optical Properties (Before and After Testing):

The optical properties are a function of the injected charge density (Q). For these devices it is Q=CExOD, where the coloration efficiency (CE) is 48 cm^2/C and optical density is defined as OD = log (T_o/T_t) for a specified wavelength.

Analytical Methods:

Spectrophotometry, cyclic voltammetry.

Degradation or Failure Modes:

(1) A gradual decrease in injected charge per unit area (mC/cm^2) is seen after 10^4 cycles, this is thought to be caused by an ion exchange reaction occuring at the hydroxyl sites in the WO_3 layer. The injected charge level begins at 10 mC/cm^2 and declines to 6 mC/cm^2 after 10^5cycles.

(2) The effect of higher temperature caused the device to slow down and the charge injection declines. After a few days a constant level was achieved. The injected charge starts at about 16 mC/cm^2 and drops to 14 mC/cm^2 at RT. At 90 C the injected charge becomes constant at 6 mC/cm^2.

(3) A durability cycling test comparing indoors and outdoors showed that the device response (injected charge) decreases with time. Outdoors this is probably caused by UV photochromism of the WO_3 material. The injected charge begins at 16 mC/cm^2. Indoors this level declines to 9 mC/cm^2 after 10^5 cycles. Outdoors this level drops to about 7 mC/cm^2 after 10^5 cycles.

(4) The results of the Weather-O-Meter exposure were compared to outdoor reponses. The injected charge for a 10x10 cm^2 device began at 16 mC/cm^2 and after 2000 hours dropped to 10 mC/cm^2. For a 30x30cm^2 device, it begain at 10 mC/cm^2 and dropped to 7 mC/cm^2 after 2000 hours of exposure. Some saturation is seen after 1000 hours.

Throughout most of the (1-4) tests the coloration efficiency remained unchanged at about 45-48 cm^2/C. In the outdoor exposure tests the CE fell the most to 42 cm^2/C.

References:

J. Nagai, T. Kamimori and M. Mizuhashi, " Transmissive Electrochromic Device", Solar Energy Materials, 14(1986)175. and

J. Nagai, T. Kamimori and M. Mizuhashi,"Mechanism of Long Term Change in Electrochromism of Li_xWO_3 Films" Proc. SPIE 502(1984)59.

REFERENCE REPORTING SHEET

ID-Code: A-4 **Number:**17

Reporters Name: C. M. Lampert **Ref. Date:** 1987

Coating/Substrate: Glass/ITO/a-WO_3/$LiClO_4$-Redox/ITO/glass, produced by e-beam evaporation at RT. Redox reagents are mixed into the electrolyte for the counter electrode.

Manufacturer: Asahi Glass Co, Yokohama, Japan

Load: (1) Cyclic Voltage at RT and 100 C. (2) storage at different temperatures (3) cycling under indoor and outdoor conditions (4) accelerated simulated weathering.

Test Procedure:

(1) Color/bleaching cycles were carried out using a D.C. potential of 1.0V or-1.0V for a 3 min interval. Over 10^5 cycles were performed. A 30x30 cm^2 device was used.

(2) Cells were cycled for 1 min. intervals under different temperatures of, RT, 50, 60, 90 C , for over 30 days. The device was 10x10 cm^2 in size.

(3) Color/bleaching cycles were done outdoors using a D.C. potential of 1.0V or -1.0V for a 1 min. interval. Over 10^5 cycles were performed. A 10x10 cm^2 device was used.

(4) A device was cycled in a Weather-O-Meter at 60 C with an exposure to a carbon arc lamp for over 2000 hrs. Both 10x10cm^2 and 30x30 cm^2 devices were tested.

Optical Properties (Before and After Testing): See comments

Analytical Methods:

Spectrophotometry, cyclic voltammetry.

Degradation or Failure Modes:

(1) As the device cycles Li^+ions accumulate in the WO_3 film and the emf shifts in the cathodic direction. This results in a gradual decrease in injected charge . Also, reduction of the ITO layer may cause this effect. ITO has a reduction potential of -1.0to -2.5V (vs SCE) depending on the pH of the electrolyte.

(2) The effect of higher temperature caused the device to slow down and the charge injection declines. After a few days a constant level was achieved. The injected charge starts at about 16 mC/cm^2 and drops to 14 mC/cm^2 at RT. At 90 C the injected charge becomes constant at 6 mC/cm^2.

(3) The durability cycling test between indoors and outdoors showed that the device response (injected charge) decreases. This is probably caused by UV photochromism of the WO_3 layer or photoelectrolysis on the ITO or WO_3 electrode surfaces. Also, outdoor exposure showed lowering of coloration efficiency beyond 10^3 cycles. The change in injected charge density with time dropped the greatest for the highest injected charge levels.

Comments: This paper is an updated version of: J. Nagai, T. Kamimori and M. Mizuhashi, " Transmissive Electrochromic Device", Solar Energy Materials, 14(1986)175. It also contains data on reflective devices. Please refer back to the reporting sheet for this former reference for further details.

Reference:

T. Kamimori, J. Nagai and M. Mizuhashi, " Electrochromic Devices for Transmissive and Reflective Light Control" Solar Energy Materials 16(1987)27.

REFERENCE REPORTING SHEET

ID-Code: J-1 **Number:**19

Reporters Name: C. M. Lampert **Ref. Date:**1987

Coating/Substrate:ITO/NiO_xH_y/KOH/Pt, the device was 1.5x2.0 cm in size. The NiO film was produced by R.F. Magnetron Sputtering.

Manufacturer: Chalmers University of Technology, Physics Dept., Gothenburg, Sweden.

Load: Cyclic Voltammetry

Test Procedure: Cyclic voltammetry was carried out using 1.35V to -0.95 V potential with a cycle time of 30 s. for $2x10^4$ cycles.

Optical Properties (Before and After Testing):

A small positive change was noted in the bleached luminous transmittance with cycling aprox. 72%->75% after 10^4 cycles. The colored luminous transmittance was T=12% after 10^4 cycles.

Analytical Methods:

Cyclic voltametry and ^{15}N nuclear reaction analysis.

Degradation or Failure Modes:

No specfic failure mode was identified.

Reference:

J.S.E.M. Svensson and C. G. Granqvist, " Electrochromism of Nickel-Based Sputtered Coatings" Solar Energy Materials , 16(1987)19

REFERENCE REPORTING SHEET

ID-Code: H-1 **Number:**24

Reporters Name: C. M. Lampert **Ref. Date:**1982

Coating/Substrate:(1)glass/ITO/a-WO_3/MgF_2/Au and (2) glass/ITO /MgF_2 / a-WO_3/ Au. The device area was $0.1cm^2$

Manufacturer: Fujitsu Laboratories, Kawasaki, Japan

Load: Effect of moisture on cycling performance.

Test Procedure:

Studied the effect of device cycling in the ambient atmosphere. Driving voltage was +/- 3V and +/-2.8V at 0.1Hz. Optical properties were monitored

Optical Properties (Before and After Testing):

Change in optical density was measured as a function of applied voltage.

At 3V a change of OD= 0.6 for 8 s for device (1). For device (2) a change of 0.3 for 8 s was noted. For an optical density change of OD=0.4 the number of water molecules needed are $2x10^{16}/cm^3$ which is the amount in the MgF_2 layer. For the higher optical densities the water must come from the atmosphere.

Analytical Methods:

Change in optical density measured with He-Ne laser, 624 nm. Distribution of water in the device was measured with an ion microanalyzer. Gas boubles were detected by an optical microscope.

Degradation or Failure Modes:

It is concluded that half of the water need for the device operation came from the ambient atmosphere. During coloration this water is dissociated at the Au interface. During bleaching gas bubbles are observed at the Au interface at -1V potential. This indicates that bleaching is not dependent on the dissociation of water.

Reference:

T. Yoshimura, M. Watanabe, K. Kitota and M. Tanaka, "Electrolysis in Electrochromic Device Consisting of WO_3 and MgF_2 Thin Films", Jap. J. of Appl. Phys. 21(1982)128.

REFERENCE REPORTING SHEET

ID-Code: I-1, I-2 **Number:**28,29

Reporters Name: C.M. Lampert **Ref. Date:** 1984

Coating/Substrate: ITO/a-WO_3/a-SiO_2/Au, prepared by vacuum evaporation, the ITO was prepared by D.C. Sputtering.

Manufacturer: Solid State Physics Institute, Latvian State Univ. Riga, USSR.

Load: (1) Slow linear voltage sweep with and without a small superimposed A.C. voltage, and current and voltage pulses.

Test Procedure: (1) Bias voltage linear sweep analysis, -2.5 to 2V. The A.C. Voltage was 10 mV and ranged from 20-10^5 Hz. The conditions were RT with humidity of 40%.

Optical Properties (Before and After Testing): not available

Analytical Methods:

Lock -in vector voltmeter, audio generator, bias linear voltage generator,
light source, modulators and detector.

Degradation or Failure Modes:

(1) The coloration and bleaching process was studied. The gold interface serves as a surface for catalytic dissociation for water. When the device voltage exceeds 1.3V, a hydroxide layer is formed on the gold surface following: $Au + 3OH^- \text{--->} Au(OH)_3 + 3e^-$. At this stage coloration takes place in the WO_3 layer. Above 1.6V the threshold for oxygen discharge is reached. On the negative current cycle, at 0.8 V the reduction of gold hydroxide occurs and bleaching begins . At -0.1V water is reformed. Final bleaching of the WO_3 film is observed at -0.4V . At -3V oxygen evolution occurs. The presence of water in this device is important to its operation and the gold layer serves as a catalytic surface. The A.C. analysis shows the device behaves as as series resistance between the ITO an Au layers separated by a parallel circuit of a capacitor and resistor signifying the WO_3 layer.

Comments: For many years it was thought that this device did not require water to function. This work clarifies the reactions occuring in the device showing the important significance of water for this device to function. The gold layer serves as a catalytic surface.

References:

A.R. Lusis, J.J. Kleperis, A.,A. Brishka, and E.V. Pentyush, "Electro-optic Spectroscopy of Electrochromic Processes in Tungsten Trioxide", Solid State Ionics 13(1984)319.

A.R Lusis, Y.K. Klayavin, Y.Y. Kleperis,Y.Y. Pinnis and O.A, Rode," Electrochemical Processes in Solid Electrochromic Systems" Elektrokhimiya 18(1982)1538.

APPENDIX B

STABILITY AND AGING OF SELECTIVE ABSORBER COATINGS

Reference Reporting Sheet

ID-Code: A1 Number: 1
Reporters Name: U. Frei Ref. Date: 1983
Coating/Substrate: Black chrome on 304 stainless steel
Load: Constant temperatures: 300 °C, 450 °C
Test Procedure: Tests in air for 24, 50 and 100 hours
Optical Properties: (before and after testing)

Heating temp. and test duration	ϵ	α_s
as prepared	0.15	0.89
300 °C; 25 h	0. 14	0.83
450 °C; 24 h	0.14	0.78
450 °C; 50 h	0.12	0.74
450 °C; 100 h	0.13	0.77

Analytical Methods: SEM, AES

Degradation Modes: AES studies have indicated that chromium oxide acts as a diffusion barrier, and remains fairly thermally stable against diffusion and therefore against oxidation. After 24 hr at 450 °C, no additional changes could be observed.

Comments:

These studies are a part of a paper comparing different substrate materials: nickel, gold, copper, stainless steel, chromium.

Reference:

D. Bacon; A. Ignatiev, "The role of the substrate in the optical degradation of solar absorbing black chrome." Solar Energy Materials 9 (1983) 3-19.

Reference Reporting Sheet

ID-Code: A1 Number: 2
Reporters Name: Köhl Ref. Date: 1985
Coating/Substrate: Black chrome on mild steel
Production: Laboratory (electroplated + thermally oxidized)
Test Procedure: Constant temperature in air
Load: Constant temperatures: 300, 500 °C
Analytical Methods: Spectral reflectance (0,4 - 2, 5 μm), SEM
Failure Mode:
Optical Properties: (before and after testing)

	as dep.	500C, 64h	as deposited	350C, 1048h
α_s	0.907	0.905	α_s: 0.920	0.918
ϵ (T)	unchanged (approx. 0.11)		ϵ (80°): 0.141	0.155

Degradation Modes:

Growth of the chromium oxide layer (~ 0,1μm)
(shifts reflectance minimum to the infrared)

Comments:

Not considered a cermet treatment as interference layer of a semiconductor and metal (but SEM shows slight roughness)

Reference:

K. J. Cathro, "Oxidized chromium as a selective surface," Solar Energy, 35, 4 (1985) 381-384.

ID-Code: A1

Number: 3

Reporters Name: M. Kohl

Coating/Substrate: Black chrome on 321 stainless steel

Manufacturer: MAN (FRG) by chemical vapor deposition

Load: Constant temperatures in air

Test Procedure: 600C for up to 1000 h

Optical Properties: (before and after testing)

	as deposited	100h 600C	500h 600C	1000h at 600C
α_s	0.94	0.91	0.89	0.9
-				
ϵ	0.27	0.18	0.13	0.18

Analytical Methods:

Spectral reflectance (0.36 - 40 μm), AES, X-Ray analysis, SEM

Degradation Modes:

Oxidation at the stainless steel surface was suggested.

Comments:

Layer consists on pure Cr_2O_3 (very rough surface)
Work appears incomplete

Reference:

E. Erben et al., "CVD black chrome coatings for high temperature photothermal energy conversion", Solar Energy Materials, 12 (1985) 239 - 248.

ID-Code: A3

Number: 1

Ref. Date: 1985

Reporters Name: Köhl

Coating/Substrate: Black chrome (CVD) on 321 stainless steel

Manufacturer: MAN (FRG) by CVD

Load: Cyclic temperatures in air

Test Procedure: 12 h room temperature and
12 h high temperature (500 °C) for 100 h total cycle.

Optical Properties: (before and after testing)

	as deposited	500C	550C
α_s	0.94	0.95	0.94
ϵ	0.32	0.28	0.23

Analytical Methods:

Spectral reflectance (0.36 - 40 μm), AES, X-Ray analysis

Comments:

Layer consists of pure Cr_2O_3 (very rough surface) Work seems to be incomplete

Reference:

E. Erben et al., "CVD black chrome coatings for high temperature photothermal energy conversion", Solar Energy Materials, 12 (1985) 239 - 248.

ID-Code: B1

Number: 1

Reporters Name: M. Köhl, Stuttgart, FRG

Ref. Date: 1982

Coating/Substrate: Black chrome on nickel on copper on aluminium

Manufacturer: Olympic Plating Company

Load: 90C temperature for 1250, 3000, 4800 h

Test Procedure: Dry circulating air oven

Optical Properties: (before and after testing) Increase of NIR-reflectance

	as deposited	1250 hr., 90C	4800, 90C
α_s	0.9411	0.934	0.938
ϵ	0.115	0.113	

Analytical Methods:

VIS/NIR-Spectroscopy SEM, X-Ray Diffraction, AES, XPS

Degradation Modes:

Reduction of Cr^{6+} to Cr^{3+} with more pronounced nodular surface morphology

Reference:

R.A. Osiecki, Evaluation of Selective soar absorber coatings, Phase II, Final Technical Report, LMSC-D876763 (1982) Lockheed Report, USA

ID-Code: B1

Number: 2

Reporters Name: U. Frei

Ref. Date: 1979/80

Coating/Substrate: Black chrome on nickel on aluminium

Manufacturer:

Load: Constant temperature: 350C for 24, 134 hr.

Test Procedure: Tests in air

Optical Properties: (before and after testing)

	As deposited	24 h,350C	134h, 350C
α_s	0.98	0.88	0.84
ϵ	0.20	0.11	0.08
134 h	0.84	0.08	

Analytical Methods: SEM, TEM

Degradation Modes:

The thermal degradation proceeds by a change in the shape of the chromium oxide particles from their initial needle-like structure to a more spherical shape. This structural change occurs as the particles dry to minimize their surface energy by transforming into spheres.

Reference:

Thermal Degradation of chronium black solar selective absorbers. I.T. Ritchie; S.K. Sharma; J. Valignat; J. Spitz Solar Energy Materials 2; (1979/80); 167-176.

ID-Code: B1 Number: 3

Reporters Name: U. Frei Ref. Date: 1984

Coating/Substrate: Black chrome on nickel

Production: Harshaw

Test Procedure Constant temperature in air (200° - 450C)

Analytical Methods: AES

Failure Mode:

Optical Properties: (before and after testing):

	As dep.	50h/450C	235 h/450°C
α_s	0.98	0.952	0.892
ϵ (300°C)	0.31	0.175	0.156

Decomposition:

Outgassing:

Degradation Modes:

The thermal degradation proceeds by a change in the shape of the chromium oxide particles from their initial needle-like structure to a more spherical shape. This structural change occurs as the particles dry to minimize their surface energy by transforming into spheres.

Comments:

The data were used to define the solar absorptance as a function of film oxide content. In addition optical reflectance calculations based on the Maxwell-Garnett theory are included in the paper.

Reference:

I.N. Sweet, R.B. Pettit and M.B. Chamberlain, Solar Energy Mat. *10* 1984, 251-286. "Optical modeling an aging characteristics of thermally stable black chrome solar selective coatings."

ID-Code: B1 Number: 4

Reporters Name: U. Frei Ref. Date: 1982

Coating/Substrate: Black chrome /Nickel

Manufacturer: Tetrachromate^R

Load: Constant temperatures: 275°C/350°C

Test Procedure: Tests in air

Optical Properties: (before and after testing)

The paper includes graphs of the absorptions and transmittances of black chrome deposits as a function of plating time. One example for the plating time 36 sec:

	as deposited	1000 hr,275C	1000 h,350C
α_s	0.97	0.97	0.94
ϵ	0.07	0.06	0.05

Analytical Methods: SEM

Degradation Modes:

The very rapid deposition of black chrome from the tetrachromate bath, may, imply that the surface particles are originally metallic with no "protective" oxide or polymeric coatings and also consequently susceptible to oxidation. The air aged samples shows a combination of oxidation and particle growth (surface energy reducing).

Comments:

In the same paper is also some information about photothermal aging; constant temperature aging in vacuum and the results of some QUV tests.

Reference:

Black chrome selective surface. Degradation at elevated temperatures. P.M. Driver and P.G. McCormick; Solar Energy Materials 6 (1982) 381-402.

ID-Code: B1 Number: 5

Reporters Name: U. Frei Ref. Date: 1982

Coating/Substrate: Black chrome/Nickel

Manufacturer: Econochrome^R

Load: Constant temperatures: 275 °C/350 °C

Test Procedure: Tests in air

Optical Properties: (before and after testing)

The paper includes graphs of the absorptances and emittances of black chrome deposits as a function of plating time. One example for the plating time 90 sec:

	as deposited	1000 hr, 275C	1000 h, 350C
α_s	0.98	0.98	0.96
ϵ	0.07	0.07	0.07

Analytical Methods: SEM

Degradation Modes:

Degradation of the optimal plated Econochrome deposits was small. The structural changes were limited to a rounding of the previously slightly crystalline particles and also a decay of the larger complex compounds to smaller more stable substances. Alternatively, oxidations to volatile Cr^{6+} compounds and the subsequent loss of these constituents could also potentially cause the observed changes.

Comments:

In the same paper is also some information about: photothermal aging; constant temperature aging in vacuum and the results of some AQUV-tests.

Reference:

Black chrome selective surface. Degradation at elevated temperatures. P.M. Driver and P.G. McCormick; Solar Energy Materials 6 (1982) 381-402; North Holland Publishing Company.

ID-Code: B1 Number: 6

Reporters Name: U. Frei Ref. Date: 1982

Coating/Substrate: Black chrome/Nickel

Manufacturer: Chromonyx^R

Load: Constant temperatures: 275C, 350C test time 1000 h

Test Procedure: Tests in air

Optical Properties: (before and after testing)

The paper includes graphs of the absorptances and emittances of black chrome deposits as a function of plating time. One example for the plating time 200 sec:

	as deposited	1000 h,275C	1000h, 350C
α_s	0.97	0.96	0.86
ϵ	0.05	0.05	0.04

Analytical Methods:

The coated samples were examined by scanning electron microscopy.

Degradation Modes:

The particle sizes were essentially unchanged; it is probable that compositional changes are responsible for the observed deviations in the optical properties. The porosity of the coating could enable oxygen penetration into the depth. This causes oxidation of the surface and subsurface particles, changing the fill factors of metallic and dielectric constituents, as well as potentially changing the dielectric constants of the dielectric medium.

Comments:

There is also the same information about photothermal aging; constant temperature aging, in vacuum and same AQUV-tests in the paper.

Reference:

Black chrome selective surface. II. Degradation at elevated temperatures. P.M. Driver and P.G. McCormick; Solar Energy Materials 6 (1982) 381-402; North-Holland Publishing Company.

ID-Code: B1 Number: 7

Reporters Name: U. Frei Ref. Date: 1979

Coating/Substrate: Black chrome/nickel

Manufacturer: Harshaw Chromonyx^R

(trivalent chromium concentration: 16, 12 and 8 g/l Cr^{3+}

Load: constant temperature: 250C, 350C, 400C for 40, 157, 1595, 3900 h.

Test Procedure: tests in air using laboratory tube furnaces

Optical Properties (before and after testing):Temperature 350 °C

	16g/l Cr^{3+}		12g/l Cr^{3+}	
	as plated	64h,350C	as plated	3908h,350C
α_s	0.95	0.89	0.97	0.95
$\epsilon(1000)$	0.09	0.07	0.21	0.16

	12g/l Cr^{3+}	
	as plated	3908h,350C
α_s	0.97	0.98
$\epsilon(1000)$	0.29	0.07

Analytical Methods:

The coating composition and structure have been studied using transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Auger sputtering profiling.

Degradation Modes:

After heating in air to 350 °C, the major change in the coatings is an oxidation of some of the metallic chromium to Cr_2O_3.

Comments:

The thermal stability of the described black chrome coatings is strongly influenced by the Cr^{3+} concentration in the bath.

Reference:

Thermal Aging Characteristics of Electrodeposited Black chrome Solar Coatings; R.B. Pettit and R.R. Sowell; Sun II, Pergamon Press, Volume Three. (1979).

ID-Code: B1 Number: 8

Reporters Name: M. Köhl, Stuttgart, FRG Ref. Date: 1982

Coating/Substrate: Black Chrome on Nickel on Copper

Manufacturer: Highland Plating Company

Load: Temperature 90 °C for 1250, 3000,4800 h

Test Procedure: Dry circulating air oven

Optical Properties:

	as deposited	1250h, 90 C	3000h, 90C	4800h, 90C
α_s	0.95	0.95	0.93	0.94
ϵ	0.11	0.12	-	0.12

Degradation Modes:

Reduction of Cr^{6+} to Cr^{3+} during heat treatment.

Comments:

A more pronounced nodular surface morphology appears after heat treatment.

Reference:

R.A. Osiecki, Evaluation of Selective Solar Absorber Coatings, Phase II, Final Technical Report, LMSC-D876763 (1982) Lockheed Company, USA

ID-Code: B1 Number: 9

Reporters Name: M. Köhl, Stuttgart, FRG Ref. Date: 1982

Coating/Substrate: Black chrome on nickel on copper

Manufacturer: Olympic Plating company

Load: temperature 90 °C for 1250, 3000, 4800 h

Test Procedure: Dry circulating air oven

Optical Properties (before and after testing): decrease of NIR reflectance

	as deposited	1250h, 90C	3000 h, 90C	4800 h, 90C
α_s	0.971	0.965	0.967	0.969
ϵ	0.200	0.200	-	0.189

Analytical Methods:

VIS/NIR-Spectroscopy, SEM, X-Ray diffraction, AES, XPS

Degradation Modes:

Reduction of Cr^{6+} to Cr^{3+}, Oxidation of Cr to Cr^{3+} and formation of nodular surface morphology.

Reference:

R. A. Osiecki, Evaluation of Selective Solar Absorber Coatings, Phase II, Final Technical Report, LMSC-D876763 (1982). Lockheed Co. USA

ID-Code: B1 Number: 10

Reporters Name: M. Köhl Ref. Date: 1982

Coating/Substrate: Black chrome on nickel on copper foil

Manufacturer: Berry Solar Products

Load: temperatures 90 °C for 1250, 3000, 4800 h

Test Procedure: Dry circulating air oven

Optical Properties: (before and after testing):

	as deposited	1250h,90C	3000h,90C
α_s	0.950	0.947	0.950
ϵ	0.098	0.102	-

Analytical Methods:

VIS/NIR-Spectroscopy, SEM, X-Ray Diffraction, AES, XPS

Degradation Modes:

Reduction of Cr^{6+} to Cr^{3+} more pronounced nodular surface morphology

Comments:

Temperature load not high enough

Reference:

R.A. Osiecki, Evaluation of Selective Solar Absorber Coatings, Phase II, Final Technical Report, LMSC-D876763 (1982).

ID-Code: B1 Number: 11
Reporters Name: M. Köhl Ref. Date: 1985
Coating/Substrate: Black chrome on nickel stainless steel
Manufacturer: MAN (FRG) by CVD
Load: Temperature
Test Procedure: Heating in air

Optical Properties: (before and after testing):

	as deposited.	100h,600C	500h,600C	1000h,600C	1000h,500C	100h,550C
α_s	0.94	0.95	0.96	0.95	0.96	
ϵ	0.13	0.57	0.54	0.59	0.19	0.59

Analytical Methods:

Spectral reflectance (0.36 - 40 μm), AES, X-Ray analysis, SEM

Degradation Modes:

thermal oxidation of Ni layer

Comments:

Layer consists on pure Cr_2O_3r (strongly rough) Work seems to be imcomplete

Reference:

E. Erben et al., "CVD black chrome coatings for high temperature photothermal energy conversion", Solar Energy Materials, 12 (1985) 239-248.

ID Code: B 1 Number: 12
Reporter's Name: Kohl Ref. Date: 1982
Coating/Substrate: Black Chrome on Ni.
Manufacturer: Harshaw Chromonyx.
Load: Constant - temperature in a furnace: 250 °C - 500 °C.
Test Procedure: Short heating in air: 20min.
Optical Properties (before and after testing):

Analytical Methods:

SEM, AES.

Degradation Modes:

Oxidation of Cr. Diffusion of Ni.

Comments:

Comparison with solar heating (B5-2) and irradiation heating in vacuum (B6-1).

Reference:

A. Ignatiev, G. Zajac and G.B. Smith, "Solar absorber stability under high solar flux," *SPIE*, Vol. 324, (1982) 170-175.

Reference Reporting Sheet

ID Code: B 1 Number: 13
Reporter's Name: U. Frei Ref. Date: 1980
Coating/Substrate: Black Chrome on Ni.
Manufacturer: Harshaw Chromonyx.
Load: Thermal
Test Procedure:
Constant temperature in air up to 400°C for 24h.

Optical Properties (before and after testing):

	As deposited	2h, 320C	24h, 400C
			+6h, 450C
α_s	0.94	0.93	0.83
ϵ (300C)	0.08	0.07	0.06

Analytical Methods:

AES (valence balance AES), SIMS, XPS, TDS.

Degradation Modes:

The degradation is a two-step process: During the first step, at low temperatures, the deposited hydroxides are reduced to oxides with desorption of H_2O and H_2. The second step is high temperature oxidation of the fine chromium crystallites to Cr_2O_3.

Comments:

Many data and graphs for different analytical methods and a model of the particulate coating are included in the paper.

Reference:

A. Ignatiev, G.B. Smith and G. Zajac, "Refinement of solar absorbing Black chrome microstructure and its relationship to optical degradation mechanisms," *II. Applied Physics,* 51 (10), October 1980.

Reference Reporting Sheet

ID Code: B 1 Number: 14
Reporter's Name: U. Frei Ref. Date: 1980
Coating/Substrate: Black Chrome on Ni.
Manufacturer: Harshaw Chromonyx.
Load: Thermal
Test Procedure
Constant temperature in air at 350°C to 400°C.

Optical Properties (before and after testing):

	As deposited	60h,350C	60h,low Cr^{+3}	60h,350C,
			as deposited	
α_s	0.95	0.89	0.97	0.97
ξ(300°C)				

Analytical Methods:

SEM.

Degradation Modes:

Reduction of the hydroxide phase. Oxidation of the chromium metal particles. Oxidation of the substrate and diffusion of the substrate into the film.

Comments:

Also information about Black Cobalt is included in the paper.

Reference:

G.B. Smith and A. Ignatiev, "The relative merits of Black Cobalt and Black Chrome as high temperature selective absorbers," *Solar Energy Materials* 2, (1980) 461-467.

Reference Reporting Sheet

ID Code: B 1 Number: 15

Reporter's Name: C.M. Lampert

Coating/Substrate: Black Chrome on Ni plated copper.

Manufacturer: Harshaw Chemical Co.

Load: 1 hr at 200 °C, 300, 400, 500, 600 °C
in air and encapsulated under 1.3 $\times 10^{-4}$ Pa, also in-situ in electron microscope with hot stage.

Optical Properties (before and after testing):

Integrated Absorptance and Emittance (27 °) for Heat Treated Black Chrome (Values Rounded).

Heat Treatment	Vacuum		Air	
	a_i	e_i	a_i	e_i
none, as plated	0.93	0.12	0.93	0.12
200 °C, 1 hour	0.93	0.11	0.93	0.11
300 °C, 1 hour	0.93	0.11	0.93	0.09
400 °C, 1 hour	0.94	0.12	0.93	0.10
500 °C, 1 hour	0.92	0.08	0.90	0.07
600 °C, 1 hour	0.80	0.08	0.73	0.10

Analytical Methods:

SEM, Energy Dispersion X-ray Analysis, Transmission Electron Microscopy and Spectral Reflectance.

Degradation Modes:

Oxidation of metallic chromium to Cr_2O_3, diffusion of oxygen/chromium and densification of coating, grain growth of Cr_2O_3 phase, outgassing. Large changes seen at 400 ° and 500 °C, severe changes at 600 °C.

Reference:

C.M. Lampert, "Thermal Degradation of a Black Chrome Solar Selective Absorber Coating: Short Term," *Proc. of ISES*, Atlanta, GA, USA (1979) 1126.

C.M. Lampert and J. Washburn, "Microstructure of a Blackchrome Solar Selective Absorber," *Solar Energy Mat.* 1 (1979) 81.

Reference Reporting Sheet

ID Code: B 1 Number: 16

Reporter's Name: C.M. Lampert

Coating/Substrate: Black Chrome on Ni plated copper.

Manufacturer: Harshaw Chemical Co.

Load: 100 hrs. at 300 °C, 400, 500 °C
in air and encapsulated under 1.3 $\times 10^{-4}$ Pa.

Optical Properties (before and after testing):

Integrated Absorptance, Emittance and Total Normal Emittance (27 °C) for Heat Treated Black Chrome

Treatment	Air			Vacuum		
	a_i	e_i	e_{tn}	a_i	e_i	e_{tn}
None as plated	0.94	—	0.11	0.94	—	0.11
300 °C, 100 hrs	0.89	0.08	0.8	0.90	0.08	0.09
400 °C, 100 hrs	0.86	0.09	0.10	0.87	0.08	0.08
500 °C, 100 hrs	0.74	0.09	0.09	0.80	0.07	0.08

Analytical Methods:

SEM, Spectral Reflectance and Transmission Electron Microscopy.

Degradation Modes:

Oxidation of metallic chromium to Cr_2O_3, diffusion of oxygen and chromium, densification of coating, grain growth of Cr_2O_3 phase. Large changes seen at 500 °C.

Reference:

C.M. Lampert, "Metallurgical Analysis and High Temperature Degradation of the Black Chrome Solar Selective Absorber," *Thin Solid Films* 72 (1980) 75.

Reference Reporting Sheet

ID Code: B 7 Number: 1
Reporter's Name: Kohl Ref. Date: 1982
Coating/Substrate: Black chrome on Ni on Cu on Al
Manufacturer: Olympic Plating Company.
Load: Humidity/temperature: 9535 / 90 °C for 1000h, 3500h, and 5000h.
Test Procedure: Desiccator cabinet in an oven.

Optical Properties (before and after testing):

	As dep:	Chromium carbide			Stainless steel carbide				
		300 °C	400 °C	500 °C	As dep:	300 °C	300 °C	400 °C	500 °C
α_s	0.99	0.91	0.86	0.84	0.94	0.93	0.91	0.86	0.85
ξ(373K)	0.030	0.030	0.055	0.075	0.032	0.032	0.032	0.04	0.05

Analytical Methods:

VIS/NIR - Spectroscopy, SEM, X-Ray diffraction, AES, XPS.

Degradation Modes:

Oxidation of Cr to Cr^{3+}. Increase of Oxygen content. Oxidation at the copper/aluminium interface. Mechanical degradation by blistering.

Reference: R.A. Osiecki, "Evaluation of Selective Solar Absorber Coatings," *Phase II, Final Technical Report,* LMSC-D876763 (1982).

Reference Reporting Sheet

ID Code: B 7 Number: 2
Reporter's Name: Köhl Ref. Date: 1982
Coating/Substrate: Black Chrome on Ni on Cu.
Manufacturer: Highland Plating Co.
Load: Humidity: 95%RH;temperature: 90C for 1000h, 3500h and 5000h.

Test Procedure: Desiccator cabinet in an oven.

Optical Properties (before and after testing):

	as deposited	1000h,90C,95%RH	3500h,90C,95%R	5000h,90C,95% RHH
α_s	0.962	0.957	0.956	0.951
ϵ	0.122	0.133	-	0.133

Analytical Methods: VIS/NIR-Spectroscopy, SEM, X-ray diffraction, AES, XPS.

Degradation Modes:

Oxidation of Cr to Cr^{3+}. Decrease of metal/oxygen ratio.

Reference:

R.A. Osiecki, "Evaluation of Selective Solar Absorber Coatings," *Phase II, Final Technical Report,* LMSC-D876763 (1982).

Reference Reporting Sheet

ID Code: B 7 Number: 3

Reporter's Name: Köhl Ref. Date: 1982

Coating/Substrate: Black Chrome on Ni on Cu.

Manufacturer: Olympic Plating Co.

Load: Humidity/temperature: 952RH, 90C for 1000h, 3500h and 5000h.

Test Procedure: Desiccator cabinet in an oven.

Optical Properties (before and after testing):

	as deposited	1000h,90C,95%RH	3500h,90C,95%RH	5000h,90C,95%RH
α_s	0.954	0.941	0.945	0.938
ϵ	0.166	0.130	-	0.123

Analytical Methods: VIS/NIR - Spectroscopy, SEM, X-Ray diffraction, AES, XPS.

Degradation Modes:

Oxidation of Cr to Cr^{3+}. Increase of metal/oxygen ratio.

Reference:

R.A. Osiecki, "Evaluation of Selective Solar Absorber Coatings," *Phase II, Final Technical Report,* LMSC-D876763 (1982).

Reference Reporting Sheet

ID Code: B 7 Number: 4

Reporter's Name: Köhl Ref. Date: 1982

Coating/Substrate: Black Chrome on Ni on Cu foil.

Manufacturer: Berry Solar Products.

Load: Humidity/temperature: 953RH/90 °C for 1000h, 3500h, and 5000h.

Test Procedure: Desiccator cabinet in an oven.

Optical Properties (before and after testing): 953 RH

	as deposited	1000h,90C	3500h,90C	5000h, 90C
α_s	0.949	0.951	0.950	0.944
ϵ	0.081	0.103		0.094

Analytical Methods: VIS/NIR - Spectroscopy, SEM, X-Ray diffraction, AES, XPS.

Degradation Modes:

Oxidation of Cr to Cr^{3+} at the surface. Increase of metal/oxygen ratio. More pronounced nodular structure. Microcracks.

Reference:

R.A. Osiecki, "Evaluation of Selective Solar Absorber Coatings," *Phase II, Final Technical Report,* LMSC-D876763 (1982).

Reference Reporting Sheet

ID Code: B 12 Number: 1
Reporter's Name: Köhl Ref. Date: 1982
Coating/Substrate: Black Chrome on Ni on Cu on Al.
Manufacturer: Olympic Plating Company.
Load: Outdoor stagnation for 9.5 months.
Test Procedure: NBS solar collector stagnation box at Palo Alto, CA, USA (37 °, 27').

Optical Properties (before and after testing):
Increase in NIR reflectance

	as deposited	9.5 months
α_s	0.924	0.937
ϵ	0.115	0.105

Analytical Methods: VIS/NIR - Spectroscopy, SEM, X-Ray diffraction, AES, XPS.

Degradation Modes:

Reduction of Cr^{6+}. Similar to dry temperature test.

Reference:

R.A. Osiecki, "Evaluation of Selective Solar Absorber Coatings," *Phase II, Final Technical Report,* LMSC-D876763 (1982), Lockheed Corp., USA.

Reference Reporting Sheet

ID Code: B 12 Number: 2
Reporter's Name: Köhl Ref. Date: 1982
Coating/Substrate: Black Chrome on Ni on Cu.
Manufacturer: Olympic Plating Company.
Load: Outdoor stagnation for 9.5 months.

Optical Properties (before and after testing):
Increase in NIR reflectance

	as deposited	9.5 months
α_s	0.962	0.970
ϵ	0.162	0.145

Analytical Methods: VIS/NIR - Spectroscopy, SEM, X-Ray diffraction, AES, XPS.

Degradation Modes:

Reduction of Cr^{3+} to Cr^{3+}. Oxidation of Cr to Cr^{3+}. Similar to dry temperature test.

Reference:

R.A. Osiecki, "Evaluation of Selective Solar Absorber Coatings," ***Phase II, Final Technical Report,*** LMSC-D876763 (1982).

Reference Reporting Sheet

ID Code: B 12 Number: 3

Reporter's Name: Köhl Ref. Date: 1982

Coating/Substrate: Black Chrome on Ni on Cu.

Manufacturer: Highland Plating Company.

Test Procedure: NBS solar collector stagnation box at Palo Alto, CA, USA (37 °, 27').

Load: Outdoor stagnation for 9-5 months.

Optical Properties (before and after testing):
Increase in NIR reflectance

	as deposited	9.5 months
α_s	0.960	0.946
ϵ	0.140	0.122

Analytical Methods: VIS/NIR - Spectroscopy, SEM, X-Ray diffraction, AES, XPS.

Degradation Modes:

Reduction of Cr^{6+} to Cr^{3+}. Similar to dry temperature test.

Reference:

R.A. Osiecki, "Evaluation of Selective Solar Absorber Coatings," *Phase II, Final Technical Report,* LMSC-D876763 (1982).

Reference Reporting Sheet

ID Code: B 12 Number: 4

Reporter's Name: M. Köhl Ref. Date: 1982

Coating/Substrate: Black chrome on nickel on copper foil

Manufacturer: Berry Solar Products

Load: Outdoor stagnation for 9.5 months

Test Procedure: NBS Solar collector stagnation box at Palo Alto (37 ° 27')

Optical Properties (before and after testing):
Increase of NIR-reflectance

Analytical Methods: VIS/NIR-Spectroscopy; SEM; X-ray diffraction; AES; XPS

Degradation Modes:

Reduction of Cr^{6+} to Cr^{3+} Similar to dry temperature test.

Reference:

R.A. Osiecki, "Evaluation of Selective Solar Absorber Coatings, Phase II, Final Technical Report" *LMSC-D876763* (1982).

Reference Reporting Sheet

ID Code: C 1
Number: 1
Reporter's Name: U. Frei
Ref. Date: 1983
Coating/Substrate: Black chrome on gold on nickel
Load: Constant temperatures: 300 °C/450 °C
Test Procedure: Tests in air for 24 hours

Optical Properties (before and after testing):

	as deposited	24h,300C	24h,450C
α_s	0.87	0.83	0.68
ϵ	0.08	0.09	0.08

Analytical Methods: SEM, AES

Degradation Modes:

The gold layer is instable to diffusion of the nickel underlayer. The diffused nickel is subsequently oxidized at the surface.

Comments:

These studies are one part of a paper comparing different substrate materials such as nickel, gold, copper, stainless steel and chromium.

Reference:

D. Bacon and A Ignatiev, "The role of the substrate in the optical degradation of solar absorbing black Chrome," *Solar Energy Materials,* 9 (1983) 3-19.

Reference Reporting Sheet

ID Code: C 1
Number: 2
Reporter's Name: U. Frei
Ref. Date: 1983
Coating/Substrate: Black chrome on copper
Load: Constant temperatures: 300 °C/450 °C
Test Procedure: Tests in air for 24 hours

Optical Properties (before and after testing):

	as deposited	24h,300C	24h,450C
α_s	0.86	0.80	0.70
ϵ	0.08	0.35	0.35

Analytical Methods: SEM, AES

Degradation Modes:

The degradation modes are not clearly discussed. After heating black chrome on copper to 300 °C poor physical and optical behavior is observed. After heating to 450 °C the AES studies show principally copper and oxygen at the surface, suggesting the formation of a "microstructure" of black copper oxide.

Comments:

These studies are one part of a paper comparing different substrate materials such as nickel, gold, copper, stainless steel and chromium.

Reference:

D. Bacon and A. Ignatiev, "The role of the substrate in the optical degradation of solar absorbing black Chrome," *Solar Energy Materials,* 9 (1983) 3-19.

Reference Reporting Sheet

ID Code: C 1 Number: 3
Reporter's Name: Köhl Ref. Date: 1979
Coating/Substrate: Black chrome on Nickel
Production: Laboratory
Test Procedure: Constant temperature 350 °C for 24h,134h in air

Optical Properties (before and after testing):

	as deposited	24h,350C	134h,350C
α_s	0.98	0.88	0.84
ϵ	0.20	0.11	0.08

Analytical Methods: Spectral reflectance (0.3-2.5μm), SEM

Degradation Modes:

Morphological changes of the Cr_2O_3 particles (from neeles to spheres)

Comments:

More detailed investigations are required.

Reference:

I.T. Ritchie S.L. Sharma, J. Valignat, J. Spitz, "Thermal Degradation of Chromium Black Solar Selective Absorbers," *Solar Energy Materials*, 2 (1979/80) 167-176.

Reference Reporting Sheet

ID Code: C 1 Number: 4
Reporter's Name: Köhl Ref. Date: 1985
Coating/Substrate: Black chrome on rhodium on nickel on stainless steel.
Manufacturer: MAN (FRG) by CVD
Test Procedure: 500 °C - 600 °C for 100h
Optical Properties (before and after testing):

	as deposited	100h,500C	100h,550C	100h,600C
α_s	0.92	0.93	0.91	0.91
ϵ	0.18	0.22	0.22	0.25

Analytical Methods: Spectral reflectance (0.36-40μm), AES, X-ray analysis, SEM

Degradation Modes:

Oxidation of Ni

Comments:

Layer consists on pure Cr_2O_3 (strongly rough). Work seems not to be completed.

Reference:

E. Erben et al., "CVD black chrome coatings for high temperature photothermal energy conversion," *Solar Energy Materials*, 12 (1985) 239 - 248.

Reference Reporting Sheet

ID Code: C 3 Number: 1

Reporter's Name: Köhl Ref. Date: 1985

Coating/Substrate: Black chrome (CVD) on rhodium on nickel on stainless steel.

Manufacturer: MAN (FRG) by CVD

Load: Cyclic temperature in air

Test Procedure: 12h room temperature; 12h high temperature (500 °C and 550 °C) for 100h

Optical Properties (before and after testing):

	as deposited	100h,500C	100h,550C
α_s	0.93	0.95	0.94
ϵ	0.16	0.22	0.22

Analytical Methods: Hemispherical reflectance (0.36-40μm), AES, X-ray analysis, SEM

Degradation Modes:

Comments:

Layer consists of pure Cr_2O_3 (strongly rough). Work seems not to be completed.

Reference:

E. Erben et al., "CVD black chrome coatings for high temperature photothermal energy conversion," *Solar Energy Materials,* 12 (1985) 239 - 248.

Reference Reporting Sheet

ID Code: D 1 Number: 1

Reporter's Name: Köhl Ref. Date: 1979

Coating/Substrate: Ni/Al_2O_3 on Ni/quartz on copper

Manufacturer: Laboratory PVD

Load: Constant temperature in vacuum and in air

Test Procedure:

Brief heating above 600 °C in vacuum (10^{-6} Torr), 300 °C, 400 °C, 500 °C, in air, maximum 1100h.

Optical Properties (before and after testing):

for copper substrate

	as deposited	50h,300C	1000h,400C	1000h,500C
α_s	0.93	0.90	0.95	0.95
ϵ				

Analytical Methods: Hemispherical reflectance (0.2-2.5μm)

Degradation Modes:

Flaking off from Cu-Substrate. Changes in the interference structure of the spectral reflectance. No problems in vacuum.

Comments:

No systematic investigation and no analysis of the degradation modes.

Reference:

H.G. Craighead et al., "Metal/Insulator composite selective absorbers," *Solar Energy Materials,* 1 (1979) 105-124.

Reference Reporting Sheet

ID Code: D 1
Number: 2
Reporter's Name: Köhl
Ref. Date: 1979
Coating/Substrate: Pt/Al_2O_3 on Pt/quartz or copper
Manufacturer: Laboratory PVD
Load: Constant temperature in air and in vacuum
Test Procedure: Brief heating in vacuum ($P = 10^{-6}$ Torr) 300 °C - 600 °C in air

Optical Properties (before and after testing):
On copper changes of α_s less than 1% at 400 °C in air. No changes on Pt/quartz at 600 °C in air stable in vacuum.
Analytical Methods: Hemispherical reflectance (0.3-2.5μm), SEM
Degradation Modes:

Flaking of the Cu-substrate at 500 °C.

Comments:

Very high temperature stability

Reference:

H.G. Craighead et al., "Metal/Insulator composite selective absorbers," *Solar Energy Materials*, 1 (1979) 105-124.

Reference Reporting Sheet

ID Code: D 1
Number: 3
Reporter's Name: Köhl
Ref. Date: 1982
Coating/Substrate: Mo/Al_2O_3 on quartz
Manufacturer: Laboratory PVD
Load: Constant temperature in air and in vacuum
Test Procedure: 750 °C, 800 °C, 880 °C in vacuum, up to 500 °C in air.

Optical Properties (before and after testing):
Decrease of α_s at 90h and 880 °C in vacuum with roughened surface stable after 2 weeks at 375 °C ($\alpha_s > 0.99$) in air. Stable after 2 weeks at 750 °C in vacuum.
Analytical Methods: Visual inspection, spectral specular reflectance (0.3-30μm).
Degradation Modes:

Oxidation of Mo starting from the boundaries of the samples.

Comments:

Very high absorptance, but no information on emittance.

Reference:

G.A. Nyberg, H.G. Craighead and R.A. Buhrman, "Surface roughness and thermal stability of graded cermet photothermal absorber coatings with very high absorptivities," *Thin Solid Films*, 96 (1982) 185-190.

Reference Reporting Sheet

ID Code: D 1 Number: 4
Reporter's Name: Köhl Ref. Date: 1982
Coating/Substrate: Pt/Al_2O_3 on quartz
Manufacturer: Laboratory PVD
Load: Constant temperature in air and in vacuum
Test Procedure: Up to 1000 °C in air

Optical Properties (before and after testing):
α_s after 1 week at 650 °C: 0.980
α_s as deposited: 0.985
α_s after 33h at 1000 °C: 0.91
α_s as deposited: 0.92

Analytical Methods: Visual inspection, spectral specular reflectance (0.3-30μm).

Degradation Modes:

None noted.

Comments:

Extremely stable at high temperatures. Very high absorptance, but no information on emittance. No adhesion problems.

Reference:

G.A. Nyberg, H.G. Craighead and R.A. Buhrman, "Surface roughness and thermal stability of graded cermet photothermal absorber coatings with very high absorptivities," *Thin Solid Films,* 96 (1982) 185-190.

Reference Reporting Sheet

ID Code: D 1 Number: 5
Reporter's Name: Köhl Ref. Date: 1986
Coating/Substrate:
Ni/MgF_2 on various substrates (Cu, Al, Mild Steel, Stainless Steel, and Ni/glass)
Manufacturer: Laboratory PVD
Load: Constant temperature in air
Test Procedure: 400 °C up to 500h.

Optical Properties (before and after testing):
Curves of α_s and ϵ (373)K as a function of ageing time.

Analytical Methods: AES, spectral reflectance (0.36-40 μm).

Degradation Modes:

For Ni/Mgf_2 on Ni on glass substitution of fluorine by oxygen. diffusion from substrate (Ni-mirror). Oxidation of the Ni-mirror.

Comments:

Stability of α_s and ξ depends on substrate. Best results for stainless steel and Ni on glass. Bad stability of thin layers with antireflection coating.

Reference:

M. Köhl, K. Gindele and M. Mast, "Accelerated ageing tests of copper-oxide and Ni–MgF_2-cermet solar absorber coatings," *Proc. of SPIE* Vol. 653 (1986) 236-242.

Reference Reporting Sheet

ID Code: E 1 Number: 1

Reporter's Name: Köhl Ref. Date: 1986

Coating/Substrate: Cr/SiO-cermet on Cu or Cr/Cu.

Manufacturer: Laboratory sputtering

Load: Constant temperature in air, argon, vacuum.

Test Procedure: 300 °C - 900 °C in air or vacuum chamber up to 28 d.

Optical Properties (before and after testing): on Cu in Air

	as deposited	400C	500C	600C
α_s	0.85	0.85	0.89	0.93
ϵ	.026	0.26		-

Analytical Methods:

X-ray diffraction, electron microprobe (ESCA), Spectral near-normal/hemispherical reflectance (0.35-20μm).

Degradation Modes:

Peeling off from the Cu at high temperatures in air. Phases of Cr_3Si and Cr_2O_3 arises.

Comments:

Reference:

L.K. Thomas et al. "Cr-SiO-cermets after high temperature treatment," *Proc. of SPIE,* 653 (1986) 202-207.

Reference Reporting Sheet

ID Code: E 1 Number: 2

Reporter's Name: Köhl Ref. Date: 1982

Coating/Substrate: Pt/Al_2O_3

Manufacturer: Laboratory sputtering

Load: Constant temperature in air.

Test Procedure: 60h at 500 °C, 16h at 750 °C.

Optical Properties (before and after testing):

Analytical Methods: Spectral reflectance (0.35-15μm), resistance measurements.

Degradation Modes:

Changes in the interference structure of the spectral reflectance. At 750 °C pitting, strong degradation and strong increase in resistance. Authors suppose diffusion from the substrate or oxidation of the substrate surface or disappearance of Pt from the surface by diffusion.

Comments:

Microanalysis would clarify the degradation modes.

Reference:

C. Sella et al., "$Pt—Al_2O_3$ selective cermet coatings for high temperature photothermal conversion," *Thin Solid Films,* 90 (1982) 425-431.

Reference Reporting Sheet

ID Code: E 2 Number: 1
Reporter's Name: Köhl Ref. Date: 1985
Coating/Substrate: Carbon/Stainless steel/copper/glass
Manufacturer: Laboratory (sputtering)
Load: Temperature
Test Procedure: Constant temperature in vacuum: 400 °C for 4h.

Optical Properties (before and after testing):
no change.

	as deposited	4h,400C
α_s	0.90	0.90
ϵ (170C)	0.05	0.05

No change in the integrated values, but of the spectrum.

Analytical Methods: Spectral reflectance (0.4-2.4μm), SIMS, TEM, X-ray diffraction, gas analysis.

Degradation Modes:

Recrystallization of the copper layer. Oxidation of the copper. Diffusion of copper and stainless steel.

Comments:

No outgassing. Very short ageing time and no high temperature.

Reference:

C. Wyon and J. Valignat, "Elaboration and characterization of a sputtered copper-stainless steel-amorphous carbon solar selective surface for use in vacuum," *Solar Energy Materials* 11 (1985) 435-446.

Reference Reporting Sheet

ID Code: E 2 Number: 2
Reporter's Name: Köhl Ref. Date: 1986
Coating/Substrate: Fe/Al_2O_3 on stainless steel.
Manufacturer: Laboratory (sputtering)
Load: Constant temperature in argon/hydrogen
Test Procedure: 400 °C, 500 °C, 600 °C for 36h.

Optical Properties (before and after testing):

Analytical Methods: Spectral reflectance (0.3-40μm)

Degradation Modes:

Pitting at 600 °C

Comments:

Not enough evaluation. No information on α_s and ϵ.

Reference:

C. Sella et al., "Low cost selective absorber based on a Fe—Al_2O_3 cermet film," *Proc. of SPIE,* Vol. 653 (1986) 208-214.

Reference Reporting Sheet

ID Code: F 2 Number: 1
Reporter's Name: Köhl Ref. Date: 1985
Coating/Substrate: Graded Al/N on Al on glass.
Manufacturer: Laboratory (react. sputtering)
Load: Constant temperature in vacuum.
Test Procedure: Heating the tubes to 300 °C - 430 °C for max 2300h.

Optical Properties (before and after testing):

	as deposited	350h,430C	2300h,390C	2300h,340C
α_s	0.92	0.97	0.92	0.93
epsilson (373K)	0.055	0.21	0.055	0.055

Analytical Methods: Heat flux measurements. Analysis of gas content.

Degradation Modes:

Outgassing of air (Activation energy 0.27 eV). Blistering due to gas bubbles.

Reference:

S.P. Chow, G.L. Harding and R.E. Collings, "Degradation of all-glass evacuated solar collector tubes," *Solar Energy Materials*, 12 (1985) 1-41.

Reference Reporting Sheet

ID Code: F 2 Number: 2
Reporter's Name: Köhl Date: 1985
Coating/Substrate: Graded stainless steel/Carbon on Cu on glass.
Manufacturer: Nitto Koh Ki (Japan)
Load: Constant temperature in vacuum.
Test Procedure: Heating all-glass collector tubes. $RT<T\leq 430$ °C for 10,000h.

Optical Properties (before and after testing):

No significant change of α_s (~ 0.90) increase of ϵ of the tube of about 1% (~ 0.06 at 373K).

Analytical Methods: Heat flux measurements. Particle pressure analyzer.

Degradation Modes:

Outgassing of CH_4, He, Ar (Activation energy 0.25 eV).

Comments:

Diffusion coefficient for Ar in the coating obeys Arrhenisus' Law Estimation of the Ar pressure and the heat loss at in-use conditions.

Reference:

S.P. Chow, G.L. Harding and R.E. Collings, "Degradation of all-glass evacuated solar collector tubes," *Solar Energy Materials*, 12 (1985) 1-41.

Reference Reporting Sheet

ID Code: F 2 Number: 3

Reporter's Name: Köhl Ref. Date: 1985

Coating/Substrate: Grades stainless steel/Carbon on Cu on glass with Al-C-F antireflection layer.

Manufacturer: Laboratory (reactive sputtering)

Load: Constant temperature in vacuum.

Test Procedure: heating the tubes to 300 °C, 340 °C, 390 °C, and 430 °C for 2800h.

Optical Properties (before and after testing):

	as deposited	2800h,300C,	2800h,340C,	2800h,390C,	2800h,430C
α_s	0.96	0.95	0.95	0.95	0.95
ϵ(373K)	0.06	0.101	0.129	0.142	0.182

Analytical Methods: Heat flux measurements.

Degradation Modes:

Greater degradation by CO, CO_2, H_2, H_2O, and CF from antireflection layer.

Comments:

Investigation not finished.

Reference:

S.P. Chow, G.L. Harding and R.E. Collings, "Degradation of all-glass evacuated solar collector tubes," *Solar Energy Materials,* 12 (1985) 1-41.

Reference Reporting Sheet

ID Code: F 2 Number: 4

Reporter's Name: Köhl Ref. Date: 1985

Coating/Substrate: MgF_2/Graded Cr/Cr_2O_3 on glass.

Manufacturer: Sunmaster (USA)

Load: Constant temperature in vacuum.

Test Procedure: Heating the tubes to 290 °C, 335 °C, and 370 °C for 4200h, and to 415 °C for 240h.

Optical Properties (before and after testing):

	as deposited	4200h,290C	4200h,335C	4200h,370C	4200h,415C
α_s	0.92	0.92	0.92	0.92	
ϵ(373K)	0.085	0.12	0.16	0.20	

Analytical Methods: Heat flux measurements, SEM.

Degradation Modes:

Microcracks. Surface agglomeration. Outgassing of He.

Comments:

Reference: S.P. Chow, G.L. Harding and R.E. Collings, "Degradation of all-glass evacuated solar collector tubes," *Solar Energy Materials,* 12 (1985) 1-41.

Reference Reporting Sheet

ID Code: F 2

Number: 5

Reporter's Name: Köhl

Ref. Date: 1983

Coating/Substrate: Stainless steel/carbon cermet on Cu on glass.

Manufacturer: Laboratory (reactive sputtering)

Load: constant temperature in vacuum.

Test Procedure: Heating absorber at 500 °C for 0.25-1h in a continuously pumped furnace ($P < 10^{-3}$Pa).

Optical Properties (before and after testing):

	as deposited	1h, 500C
α_s	0.94	0.93
ϵ (373K)	0.032	0.047

Analytical Methods: AES, spectral reflectance, spectral transmittance, X-ray analysis, hydrogen/Carbon analysis.

Degradation Modes:

None

Comments:

Further heat treatment at 375 °C for 5000h had no effect.

Reference:

S. Craig and G.L. Harding, "Composition, optical properties and degradation modes of Cu/(graded metal carbon) solar selective surfaces," *Thin Solid Films* 101 (1983).

Reference Reporting Sheet

ID Code: G 1

Number: 1

Reporter's Name: U. Frei

Ref. Date:

Coating/Substrate: Black zinc on zinc, Black zinc on galvanized steel.

Manufacturer: See ref.

Load: Constant temperature from 150 °C to 350 °C.

Test Procedure: In air, 1.0-320h.

Optical Properties (before and after testing):

	as deposited	320h,150C	320h,350C
α_s	0.97	0.97	0.88
ϵ	0.24-25	0.23	0.35

Analytical Methods: SEM, TEM, AES, RED.

Degradation Modes:

The thermal stability may be affected by the size and shape of the interface structure, the volume fraction of zinc in the interface region and the effectiveness of the zinc oxide as a barrier inhibiting oxidation. At 350 °C an oxidation of the substrate has occurred to a significant extent. (At 300 °C, no change in α_s or e_t; at 350 °C see optical properties). The result is a roughening of the film and a consequent increase of emittance.

Comments:

The anodizing parameters have been successfully modeled utilizing the technique of multiple linear regression analysis.

Reference:

J.C. Mabon and T. Inal, "Optimization and evaluation of black zinc selective solar surfaces," *New Mexico Institute of Mining and Technology,* Socorro, NM 87801 (USA).

Reference Reporting Sheet

ID-Code: G1 Number: 2

Reporters Name: M.G. Hutchins Ref. Date: 1985

Coating/Substrate: Anodically formed ZnO on leaf-zinc

Manufacturer: Dept. of Metallurgy and Materials Engineering, New Mexico Institute of Mining Technology

Load: Constant temperature in air

Test Procedure: Prolonged thermal exposure for various temperatures in the range 150°C - 400°C (in air)

Optical Properties: (before and after testing):

$\alpha > 0.97$ $\epsilon < 0.25$

α (400°C) = -0.06

Rapid degradation in α at 205°C for exposure times in excess of 700h

Analytical Methods: SEM, RED, Reflectance spectroscopy

Degradation Modes: Observed degradation attributed to sintering or dehydration and <u>not</u> oxidation of residual zinc.

Comments: Activation energy of degradation mechanism differs above and below 300°C. Degradation at lower temperatures explained by higher degradation rate in humid environments. Surfaces reported to be Zn^+ doped ZnO with graded composition and microrough surface. Interference effects observed. Effective medium modelling approach, based on Maxwell Garnett theory, applied to durability assessment.

Reference: A. Scherer and O.T. Inal, Appl. Optics <u>24</u> (20), 3348, 1985.

Reference Reporting Sheet

ID-Code: G1 Number: 3

Reporters Name: M.G. Hutchins Ref. Date: 1987

Coating/Substrate: ZnO on Zn-plated steel
ZnO on leaf-zinc

Manufacturer: Delft University of Technology

Load: Thermal aging at constant temperature in air

Test Procedure:

(i) Air heating at 80°C for two weeks
(ii) Air heating at 180°C for 1 week

Optical Properties: (before and after testing):

$\alpha_s = 0.95$ $\epsilon = 0.08$
(i) $\Delta\alpha = -0.03$ $\Delta\epsilon = +0.04$
(ii) $\Delta\alpha = -0.07$ $\Delta\epsilon = +0.39$

Analytical Methods: Reflectance spectroscopy, ion bean analysis

Degradation Modes: (i) no discussion
(ii) cause unknown - could be oxidation of Zn underlayer

Comments: Zn : 0 ratio < 1, ZnO on leaf-zinc reported to be more stable than ZnO on Zn-plated steel.

Reference: M. Van der Leij, J. Electrochem. Soc. Solid State Science and Technology <u>125</u> (8), 1361, 1978.

Reference Reporting Sheet

ID-Code: G1 Number: 4

Reporters Name: M.G. Hutchins Ref. Date: 1986

Coating/Substrate: Zinc oxide multilayer on glass

Manufacturer: University of Alberta, Canada

Load: No load specified

Test Procedure: No degradation tests reported

Optical Properties: (before and after testing):
$\alpha_s = 0.90$ $\epsilon = 0.26$

Analytical Methods: Reflectance spectroscopy

Degradation Modes: None reported

Comments:
Black zinc oxide films prepared by bias rf sputtering are overcoated with transparent, electrically conducting ZnO heat mirror films in a continuous process, achieved by altering the bias sputtering conditions. An interesting surface for future investigations. No durability results published to date.

Reference: M.J. Brett, R.R. Parsons and H.P. Baltes, Applied Optics 25 (16), 2712, 1986.

Reference Reporting Sheet

ID-Code: G1 Number: 5

Reporters Name: M.G. Hutchins Ref. Date: 1981

Coating/Substrate: Black zinc oxide on leaf zinc and
Electroplated zinc on mild steel

Manufacturer: New Mexico Institute of Mining and Technology

Load: Constant temperature heating in air

Test Procedure: Exposure for 2h in air at temperatures of 100,200, 250, and 300°C.

Optical Properties: (before and after testing):

α_s 0.96-0.97, ϵ (100°C) = 0.18-0.32

Increase in ϵ for surfaces produced on steel substrates after exposure at 300°C only. Decrease in α also observed for these samples.

Analytical Methods: SEM, TEM

Degradation Modes: Possible explanation for increase in thermal emittance is quoted as being due to lack of homogeneity and structural integrity at the zinc/steel interfaces because of the formation of Fe_xZn_y compound.

Comments: Adhesion strength and bend tests also carried out. Zinc oxide overlayers applied to leaf zinc substrates found to have better mechanical durablity.

Decrease in adhesion strength recorded an annealing temperature increased. Resistance to failure in bend test also decreases as annealing temperature is increased.

Reference: O.T. Inal, L.E. Murr, A.E. Torma and I. Gundiler, Solar Energy Materials 4 309, 1981.

Reference Reporting Sheet

ID-Code: G5

Number: 1

Reporters Name: M.G. Hutchins

Ref. Date: 1987

Coating/Substrate: ZnO on Zn-plated steel and
ZnO on leaf-zinc

Manufacturer: Delft University of Technology

Load: Ultraviolet irradiation

Test Procedure: Ultraviolet exposure with an irradiation of 120Wm^{-2} for 72h

Optical Properties: (before and after testing):

$\alpha_s = 0.95$, $\epsilon = 0.08$

$\Delta \alpha = -0.03$, $\Delta \epsilon = +0.05$

Analytical Methods: Reflectance spectroscopy, ion-beam analysis

Degradation Modes: No significant change discussed

Comments: Reference Reporting Sheet G1 No. 3

Reference: M. Van der Leij, J. Electrochem Soc. Solid State Science and Technology 125 (8), 1361, 1978.

Reference Reporting Sheet

ID-Code: H7

Number: 1

Reporters Name: M.G. Hutchins and P.R. Dolley

Ref. Date: 1985

Coating/Substrate: Fe-Mn-CuOx pigment in a silicone binder on Al substrate.

Manufacturer: Honeywell Systems and Research Centre (USA)

Load: Durability to combined indoor test procedures.

Test Procedure:
Expose samples to 30°C and 95% relative humidity for 30 days.

Optical Properties: (before and after testing):

	Before		After	
	α_s	ϵ	α_s	ϵ
Silicone, thickness sensitive	0.92	0.14	0.92	0.14
Silicone, thickness insensitive	0.89	0.38	0.87	0.39

Analytical Methods: None detailed

Degradation Modes: No discussion

Comments:
Honeywell has conducted accelerated tests on the thickness sensitive paints - emittance change of 7-12% and absorptance of 2-8% when exposed as per Fed. Test Method Std. 141, Method 6152 for 3057 hours. Optical changes from exposure to MIL-STD-810D normally less than these values.

Reference: S.W. Moore
Solar Absorber Selective Paint Research
Solar Energy Materials 12 (1985) 435-447.

Reference Reporting Sheet

ID-Code: H7 Number: 2

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1985

Coating/Substrate: Fe-Mn-CuOx pigment in a urethane binder on Al substrate.

Manufacturer: Honeywell Systems and Research Centre (USA)

Load: Durability to combined indoor test procedures

Test Procedure: Expose samples to 30°C and 955 relative humidity for 30 days.

Optical Properties: (before and after testing):

	Before		After	
	α_s	ϵ	α_s	ϵ
Urethane, thickness sensitive	0.90	0.13	0.88	0.15
Urethane, thickness insensitive	0.83	0.40	0.81	0.41

Analytical Methods: None detailed

Degradation Modes: No discussion

Comments:
Honeywell has conducted accelerated tests on the thickness sensitive paints - emittance change of 7-12% and absorption of 2-8% when exposed as per Fed. Test Method Std. 141, Method 6152 for 3057 hours. Optical changes resulting from exposure to MIL-STD-810D normally less than these values.

Reference: S.W. Moore, Solar Absorber Selective Paint Research,
Solar Energy Materials 12 (1985) 435-447.

Reference Reporting Sheet

ID-Code: H11 Number: 1
Reporter Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1987

Coating/Substrate: Polyurethanealkyd lacquer pigmented with soot sprayed on Al.

Manufacturer: Chalmers University of Technology, Goteburg, Sweden

Load: Durability to Xenon Weatherometer (as per ASTM G.27)

Test Procedure: Expose samples to Weatherometer for 1000 hours.

Optical Properties: (before and after testing):
Before α_s=0.90 ϵ=0.30

No significant change observed

Analytical Methods: None detailed

Degradation Modes: No discussion

Comments:
Optimum thickness of paint given as 0.7um. Pigment diameter detailed as being 20nm. Adhesion test (Swedish standard SIS 184171) revealed force needed to remove paint as being 0.95MN/m. Acceptable value is 0.6MN/m therefore good adhesion qualities.

Reference: S. Lofving, A Paint for Selective Solar Absorbers,
Solar Energy Materials 5 (1981) 103-105.

Reference Reporting Sheet

ID-Code: H11 Number: 2

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1985

Coating/Substrate: Fe-Mn-CuOx pigment in a silicone binder on Al substrate.

Manufacturer: Honeywell Systems and Research Centre (USA)

Load: Sequential exposure to combined indoor test procedures.

Test Procedure:

Step 1: Expose 95% relative humidity and 30° for 30 days.
Step 2: Expose to thermal cycling, 86 to 120°C for 60 cycles (duration not specified).

Optical Properties: (before and after testing):

	Before		After	
	α_s	ϵ	α_s	ϵ
Silicone, thickness sensitive	0.92	0.14	0.91	0.12
Silicone, thickness insensitive	0.89	0.38	0.87	0.38

Analytical Methods: None detailed

Degradation Modes: No discussion

Comments:
Honeywell has conducted accelerated tests on the thickness sensitive paints - emittance change of 7-12% and absorption of 2-8% when exposed as per Fed. Test Method Std. 141, Method 6152 for 3057 hours. Optical changes resulting from exposure to MIL-STD-810D normally less than these values.

Reference: S.W. Moore, Solar Absorber Selective Paint Research,
Solar Energy Materials 12 (1985) 435-447.

Reference Reporting Sheet

ID-Code: H11 Number: 3

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1987.

Coating/Substrate: Fe-Mn-CuO_x pigment in binder on Al substrate.

Manufacturer: Honeywell Systems and Research Centre (USA).

Load: Sequential exposure to combined indoor test procedures.

Test Procedure:

Step 1: Expose to 95% relative humidity and 30°C for 30 days.
Step 2: Expose to thermal cycling, 86 to 120°C for 60cycles (duration no

Optical Properties: (before and after testing):

	Before		After	
	α_s	ϵ	α_s	ϵ
Urethane, thickness sensitive	0.90	0.13	0.88	0.14
Silicone, thickness insensitive	0.83	0.40	0.79	0.47

Analytical Methods:
None detailed

Degradation Modes:
No discussion

Comments:
Severe degradation of urethane, thickness sensitive paint has occured. Investigation of causes not undertaken. Honeywell has conducted accelerated tests on the thickness sensitive paints - emittance change of 7-12% and absorption of 2-8% when exposed as per Fed. Test Method Std. 141, Method 6152 for 3057 hours. Optical changes resulting from exposure to MIL-STD-810D normally less than

these values.

Reference: S.W. Moore
Solar Absorber Selective Paint Research
Solar Energy Materials 12 (1985) 435-447.

Reference Reporting Sheet

ID-Code: H11 Number: 4

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1985

Coating/Substrate: Fe-Mn-CuOx pigment in a silicone binder on Al substrate.

Manufacturer: Honeywell Systems and Research Centre (USA)

Load: Sequential exposure to combined indoor test procedures.

Test Procedure:

Step 1: Expose to 95% relative humidity and 30°C for 30 days.
Step 2: Thermal cycling, 86 to 120°C for 60 cycles.
Step 3: Expose to 12000 equivalent sun hours

Optical Properties: (before and after testing):

	Before		After	
	α_s	ϵ	α_s	ϵ
Silicone, thickness sensitive	0.92	0.14	0.90	0.11
Silicone, thickness insensitive	0.89	0.38	0.88	0.42

Analytical Methods: None detailed

Degradation Modes: No discussion

Comments:
Honeywell has conducted accelerated tests on the thickness sensitive paints - emittance change of 7-12% and absorption of 2-8% when exposed as per Fed. Test Method Std. 141, Method 6152 for 3057 hours. Optical changes resulting from exposure to MIL-STD-810D normally less than these values.

Reference: S.W. Moore, Solar Absorber Selective Paint Research,
Solar Energy Materials 12 (1985) 435-447.

Reference Reporting Sheet

ID-Code: H11 Number: 5

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1985

Coating/Substrate: Fe-Mn-CuOx pigment in a urethane binder on Al substrate.

Manufacturer: Honeywell Systems and Research Centre (USA)

Load: Sequential exposure to combined indoor test procedures.

Test Procedure:

Step 1: Expose to 95% relative humidity and 30°C for 30 days.
Step 2: Thermal cycling, 86 to 120°C for 60 cycles.
Step 3: Expose to 12000 equivalent sun hours.

Optical Properties: (before and after testing):

	Before		After	
	α_s	ϵ	α sub s	ϵ
Urethane, thickness sensitive	0.92	0.14	0.90	0.11
Silicone, thickness insensitive	0.89	0.38	0.88	0.42

Analytical Methods:
None detailed

Degradation Modes:
No discussion

Comments:
Honeywell has conducted accelerated tests on the thickness sensitive paints - emittance change of 7-12% and absorption of 2-8% when exposed as per Fed. Test Method Std. 141, Method 6152 for 3057 hours. Optical changes resulting from exposure to MIL-STD-810D normally less than these values. Severe degradation

of urethane insensitive paint has occured making it unsuitable for active solar applications.

Reference: S.W. Moore, Solar Absorber Selective Paint Research,
Solar Energy Materials 12 (1985) 435-447.

Reference Reporting Sheet

ID-Code: H12 Number: 7

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1985

Coating/Substrate: Proprietary coating on Al sheet (Dip coated with FEP overcoat).

Manufacturer: Honeywell Systems and Research Centre (USA)

Load: Durability to outdoor testing with conditions simulating stagnation.

Test Procedure:
Expose samples in a glazed and insulated collector box such that the materials experience stagnation temperature indicative of in-service conditions under no flow.

Optical Properties: (before and after testing):

Before	$\alpha_s = 0.93$	$\epsilon = 0.18$
12 month exposure	$\alpha_s = 0.92$	$\epsilon = 0.17$
24 month exposure	$\alpha = 0.93$	$\epsilon = 0.16$

Analytical Methods: Not detailed

Degradation Modes: No discussion

Comments:
Under exposure sample temperatures reached 200°C. Samples have been returned to the test racks for continued exposure. Similar materials have been tested using different production/deposition techniques - these give similar results triangle$\epsilon = \pm$ 3% $\Delta \epsilon = \pm 1\%$.

Reference: S.W. Moore, Solar Absorber Selective Paint Research,
Solar Energy Materials 12 (1985) 449-460.

Reference Reporting Sheet

ID-Code: I1 Number: 1

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Ref. Date: 1980

Coating/Substrate: Ni in Al_2O_3 on Al

Manufacturer: Granges Aluminium, Fingspang, Sweden

Load: Durability to constant temperature in air.

Test Procedure: Exposure in air at atmospheric pressure at 300°C for 2 weeks.

Optical Properties: (before and after testing):

Initial: $\alpha_s = 0.93 - 0.96$,
$\epsilon = 0.10 - 0.20$

Following test: no significant changes registered

Analytical Methods: SEM, AES, AA

Degradation Modes: No discussion

Comments:
Further testing combining heat treatment with acidic spraying in progress at time of reporting. Paper concentrates heavily on establishment of a theoretical model based upon effective medium theories to explain selective optical response.

Reference: A. Anderson, O. Hunderi and C.G. Granquist, J. Appl. Phys. 51 (1), 754, 1980

Reference Reporting Sheet

ID-Code: I1 Number: 2

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Ref. Date: 1981

Coating/Substrate: Ni on Al_2O_3 on Al

Manufacturer: Granges Aluminium

Load: Durability to constant temperature in air

Test Procedure: Exposure at 300°C for two weeks

Optical Properties: (before and after testing):

$\alpha = 0.95$
$\epsilon = 0.15$

No change observed following test

Analytical Methods: None reported

Degradation Modes: No discussion relevant to stagnation testing

Comments: Report surface stable to other tests including exposure outdoors, solar simulator and weatherometer tests but no detailed description or numerical data presented.

Reference: G. Olssen, B. Thundal and G. Wilson, ISES Solar World Forum, Brighton, UK., Pergamon Press, 1981, pp. 163-167.

Reference Reporting Sheet

ID-Code: I1 Number: 3

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1986

Coating/Substrate: Co in Al_2O_3 on Al

Manufacturer: University of Houston

Load: Durability to elevated temperature in air

Test Procedure: Heated to 400°C for 30h in an infrared oven.

Optical Properties: (before and after testing):

$\alpha_s = 0.92$
$\epsilon = 0.26$

α remained unchanged following test although changes in form of spectral reflectance curve observed.

Analytical Methods:

AES and SEM studies show graded concentration of Co particles dispersed in porous Al_2O_3 matrix. Surface concentration of Co 5%, concentration at oxide/aluminum interface 47%.

Degradation Modes:
The loss of the interference maximum in the spectral reflectance curve following heating indicates loss of a distinct optical thickness for the overlayer. AES studies show that this principally stems from oxidation and some dispersion of the cobalt in the oxide overlayer.

Comments: High temperature stability claimed to be superior to Ni in AL_2O_3 although selectivity somewhat poorer. Stability at high temperature for more prolonged exposures (>500h) currently under investigation.

Reference: N.M. Nahar, G.H. Mo and A. Ignatiev, Solar Energy Materials 14 , 129,1986.

Reference Reporting Sheet

ID-Code: I1 Number: 4

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1987

Coating/Substrate: Ni on Al_2O_3 on Al

Manufacturer: Sunstrip International Inc.

Load: Durability to constant temperature in air

Test Procedure: Thermal exposure for each combination of 1h, 10h and 100h at temperatures of 150°C, 200°C and 300^3.

Optical Properties: (before and after testing):

$\alpha_s = 0.90$
$\epsilon = 0.09$
Only minor variations in α and ϵ recorded following tests. Modifications to the spectral reflectance curves in the uv/vis/nir observed exposures at the longest times for each temperature.

Analytical Methods:
SEM studies confirm structure of Ni particles embedded in porous Al_2O_3 matrix.

Degradation Modes: Not confirmed

Comments: Shifts in the spectral reflectance curves are consistent with a decrease in effective film thickness which increases for exposure at 100h as the temperature is increased.

Reference: M.G. Hutchins and P.R. Dolley, Durability assessment and microstructural characterisation of selective solar absorber surfaces, Proc. IEA Task X Workshop, Japan, May 1987.

Reference Reporting Sheet

ID-Code: I3 Number: 1

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1983

Coating/Substrate: Ni on Al_2O_3 on Al

Manufacturer: Indian Institute of Technology

Load: Durability to cyclic temperature in air

Test Procedure: Thermal cycling between 250°C and ambient, with 5h at each temperature, for a period of 300h

Optical Properties: (before and after testing):

Sample	Before		After	
α_s	ϵ	α_s	ϵ	
I	0.90	0.06	0.90	0.07
II	0.95	0.34	0.94	0.37
III	0.96	0.49	0.95	0.54

Analytical Methods:
SEM, TEM, AES, XPS studies conform porous nature of film and dispersion of Ni particles within the oxide film.

Degradation Modes: Surface claimed to be highly stable

Comments: Reported ϵ values high. Optical properties strongly dependent upon deposition process parameters.

Reference: S.N. Kumar, L.K. Malhotra and K.L. Chopra, Solar Energy Materials 7 , 439, 1983.

Reference Reporting Sheet

ID-Code: I5 Number: 1

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1986

Coating/Substrate: Anodically oxidised Aluminum (non-pimented)

Manufacturer: University of Houston

Load: Exposure to simulated solar radiation

Test Procedure: Exposure to high flux (1MWm^{-2}) to 400°C for various times up to 17h.

Optical Properties: (before and after testing):
No values quoted. Only minor variations observed in reflectance curves following tests.

Analytical Methods:
AES, SEM studies show a porous, rough surface. Composition of surface film as a function of depth examined in detail.

Degradation Modes: Porous oxide coating reported stable.

Comments:
Tests show stability of Al_2O_3 as a host dielectric for a metal pigmented solar absorber.

Reference: Pavlovic, T. and Ignatiev A, Thin Solid Films
138 , 97, 1986.

Reference Reporting Sheet

ID-Code: I5 Number: 2

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1986

Coating/Substrate: Co on Al_2O_3 on Al

Manufacturer: University of Houston

Load: Exposure to simulated solar radiation

Test Procedure: Exposure to high flux (1MWM^{-2}) to 400°C for 10h

Optical Properties: (before and after testing):
As reported for I1 No. 3

Analytical Methods: As reported for I1 No. 3

Degradation Modes:
Similar degredation to that reported for constant temperature exposure in an infared oven.

Comments: See I1 No. 3

Reference: N.W. Nahar, G.H. Mo and A. Ignatiev, Solar Energy Materials
14 , 129,1986.

Reference Reporting Sheet

ID-Code: I7 Number: 1

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1980

Coating/Substrate: Ni on Al_2O_3 on Al

Manufacturer: Granges Aluminium, Finspang, Sweden

Load: Durability to thermal cycling in the presence of controlled humidity.

Test Procedure: US MIL-STD-810 B : thermal cycling between 23°C and 71°C at 95% RH for 3 weeks.

Optical Properties: (before and after testing):

$\alpha_s = 0.93 - 0.96$
$\epsilon = 0.10 - 0.20$

No degradation of exposed surface observed by reflecting measurements.

Analytical Methods: SEM, AES, AA

Degradation Modes: Not discussed

Comments: Exposure test considered severe

Reference: A. Anderson, O. Hunderi and C.G. Granquist, J Appl. Phys. 51 (1), 754, 1980.

Reference Reporting Sheet

ID-Code: I7 Number: 2

Reporters Name: M.G. Hutchins and P.R. Dolley Ref. Date: 1987

Coating/Substrate: Ni on Al_2O_3 on Al

Manufacturer: Granges Aluminium

Load: Durability to thermal cycling in the presence of controlled humidity

Test Procedure: US-MIL-STD-810-B : thermal cycling between 23°C and 71°C at 95% RH for 3 weeks

Optical Properties: (before and after testing):

$\alpha_s = 0.95$
$\epsilon = 0.15$

No degredation observed by reflectance measurements

Analytical Methods:
None reported

Degradation Modes: State that subjection to extreme conditions of 100°C and 100% RH to an increase in the thickness of the Al_2O_3.

Comments: Authors also state that exposure to solutions with a low pH decreases oxide film thickness and affects Ni dispersion.

Reference: G. Olssen, B. Thundal and G. Wilson, Proc. ISES Solar World Forum, Brighton, U.K. Pergamon Press, 1981, pp. 163-167.

Reference Reporting Sheet

ID-Code: I7 Number: 3

Reporters Name: M.G. Hutchins

Coating/Substrate: Nickel pigmented aluminium oxide (Al)

Manufacturer: Sunstrip International Inc.

Load: Controlled temperature-relative humidity cucling

Test Procedure: 10 cycles of 6h at 30°C and 9515 R.H. and 6h at 60°C and 95% R.H. with a 6h transition for change of conditions. Total test time 180 h. Derivative test of MIL STD 810D

Optical Properties: (before and after testing):
$\alpha = 0.90$, $\epsilon = 0.10$ No significant change observed following test

Analytical Methods: Secondary electron microscopy, x-ray diffraction

Degradation Modes: none observed

Comments: Further testing in progress under different conditions of temperature, relative humidity and duration.

Reference: Dolley P.R. and Hutchins M.G., Accelerated testing of selective solar absorber surfaces II : Exploratory study of surface stability for exposure to a controlled temperature-humidity environment, Solar Energy Materials Research Laboratory report No. 87/7, Oxford Polytechnic, April 1987.

Reference Reporting Sheet

ID Code: K 1 Number: 1
Reporter's Name: Köhl Ref. Date: 1982
Coating/Substrate: Chromat conversion on 444 stainless steel.
Manufacturer: State Industries, Inc.
Load: Temperature: 90 °C for 1250h, 3000h, and 4800h.
Test Procedure: Dry circulating air oven.

Optical Properties (before and after testing):

	as deposited	1000h,90C	3500h,90C	5000h,90C
α_s	0.823	0.824	0.835	0.832
ϵ	0.092	0.139		0.132

Analytical Methods:
VIS/NIR spectroscopy, SEM, X-ray diffraction, AES, XPS.

Degradation Modes:
No sufficient information.

Comments:
Increase of emittance not explained.

Reference: R.A. Osiecki, "Evaluation of Selective Solar Absorber Coatings," *Phase II, Final Technical Report,* LMSC-D876763 (1982).

Reference Reporting Sheet

ID Code: K 1 Number: 2

Reporter's Name: Hutchins Ref. Date: 1987

Coating/Substrate: Skysorb - oxidized stainless steel (blue).

Manufacturer: Inco Selective Surfaces Ltd., Birmingham, U.K.

Load: Exposure to elevated temperatures in air.

Test Procedure: Exposure in air at atmospheric pressure to temperatures of 150 °C, 200 °C, and 200 °C for 1h, 10h, and 100h respectively.

Optical Properties (before and after testing):

α_s - 0.80, $\epsilon = 0.16$. No significant changes observed except for the severest these conditions, i.e. 300 °C at 100h resulted in $\Delta\alpha = -0.02$, $\Delta\epsilon = -0.04$.

Analytical Methods: Scanning electron microscopy, X-ray diffraction. No fine scale microstructure observed.

Degradation Modes:

None identified.

Comments:

At the severest condition a color change was observed. The initial blue appearance became blue-grey. A second batch of Skysorb with superior optical properties is currently under investigation. The observed decrease in ϵ following thermal exposure is of interest.

Reference:

P.R. Dolley and M.G. Hutchins, "Accelerated testing of selective solar absorber surfaces I: Exploratory study of surface stability for exposure to elevated temperatures in air," *Solar Energy Materials Research Laboratory Report No. 87/6,* Oxford Polytechnic, April, 1987.

Reference Reporting Sheet

ID Code: K 7 Number: 1

Reporter's Name: Köhl Ref. Date: 1982

Coating/Substrate: Chromat conversion on 444 stainless steel.

Manufacturer: State Industries, Inc.

Load: Humidity/temperature: 953RH/90C for 1000h, 3500h, and 5000h.

Test Procedure: Dessicator cabinet in an oven.

Optical Properties (before and after testing):

	as deposited	1000h,90C	3500h,90C	5000h,90C
α_s	0.822	0.821	0.829	0.820
ϵ	0.083	0.132	-	0.125

Analytical Methods: VIS/NIR spectroscopy, SEM, X-ray diffraction, AES, XPS.

Degradation Modes:

Not clear.

Comments:

Increase of emittance not explained.

Reference:

R.A. Osiecki, "Evaluation of Selective Solar Absorber Coatings," *Phase II, Final Technical Report,* LMSC-D876763 (1982).

Reference Reporting Sheet

ID Code: K 7 Number: 2

Reporter's Name: Hutchins Ref. Date: 1987

Coating/Substrate: Skysorb - chemically oxidized stainless steel (blue).

Manufacturer: Inco Selective Surfaces Ltd., Birmingham, U.K.

Load: Controlled temperature - relative humidity cycling.

Test Procedure: 10 cycles of 6h at 30 °C and 954 R.H. and 6h at 60 °C and 95% R.H. with a 6h transition for change of conditions. Total test time: 180h (derivative test of MIL STD 810D).

Optical Properties (before and after testing):
$\alpha_s = 0.80$, $\epsilon = 0.16$.

Analytical Methods: Secondary electron microscopy, X-ray diffraction.

Degradation Modes:

None observed.

Comments:

Further testing in progress under different conditions of temperature, humidity and duration on a second batch of Skysorb with superior optical properties.

Reference:

P.R. Dolley and M.G. Hutchins, "Accelerated testing of selective solar absorber surfaces II: Exploratory study of surface stability for exposure to a controlled temperature-humidity environment," *Solar Energy Materials Research Laboratory Report No 87/7*, Oxford Polytechnic, April, 1987.

Reference Reporting Sheet

ID Code: L 1 Number: 1

Reporter's Name: Hutchins Ref. Date: 1987

Coating/Substrate: Cobalt oxide hydroxide on nickel plated copper.

Manufacturer: In-house preparation be chemical conversion.

Load: Exposure to elevated temperatures in air.

Test Procedure: Exposure in air at atmospheric pressure to a temperature of 300 °C for 60h.

Optical Properties (before and after testing):
$\alpha_s = 0.94$, $\epsilon = 0.10$. After test, $\Delta\alpha = +0.02$; ϵ unchanged.

Analytical Methods: Scanning electron microscopy, X-ray diffraction. Post test analyses revealed compositional changes, CoO(OH) being converted to both CoO and Co_3O_4. Intrinsic absorption bands for the CoO were observed in the vis/nir reflectance spectra. visible absorptance increased, near infrared absorptance decreased.

Degradation Modes:

Oxidation of the surface coating. Some substrate oxidation was also observed.

Comments:

Initial optical properties strongly dependent on initial cobalt metal film thickness.

Reference:

M.G. Hutchins, P.J. Wright and P.D. Grebenik, "Comparison of different forms of black cobalt selective solar absorber surfaces," *Solar Energy Materials,* in press.

Reference Reporting Sheet

ID Code: L 1 Number: 2

Reporter's Name: Hutchins Ref. Date: 1987

Coating/Substrate: Cobalt oxide on nickel plated copper.

Manufacturer: In-house preparation by thermal oxidation of cobalt metal in air at elevated temperatures.

Load: Exposure to elevated temperatures in air.

Test Procedure: Exposure in air at atmospheric pressure to temperatures of 400 °C for 192h.

Optical Properties (before and after testing):
$\alpha_s = 0.96$, $\epsilon = 0.08$. Following test, $\Delta\alpha_s = -0.01$, $\Delta\ \epsilon = +0.04$.

Analytical Methods: Scanning electron microscopy, X-ray diffraction. Surface microstructure of cylindrical rods and elongated platelets with many surface voids and cavities.

Degradation Modes:

Substrate oxidation.

Comments:

Initial optical properties strongly dependent on initial cobalt metal film thickness. Surface formed by oxidation in air at 400 °C for 32h. Coating appears stable once fully oxidized but substrate oxidation prevents coating stability. Seek alternative substrate.

References:

M.G. Hutchins, P.J. Wright and P.D. Grebenik, "Comparison of different forms of black cobalt selective solar absorber surfaces," *Solar Energy Materials,* in press.

Reference Reporting Sheet

ID Code: M 1 Number: 1

Reporter's Name: Hutchins Ref. Date: 1987

Coating/Substrate: Maxorb - Black Ni foil adhered to an aluminum substrate.

Manufacturer: Inco Selective Surfaces Ltd., Birmingham, U.K.

Load: Exposure to elevated temperatures in air.

Test Procedure: Exposure in air at atmospheric pressure to temperatures of 150 °C, 200 °C and 300 °C for 1h, 10h, and 100h, respectively.

Optical Properties (before and after testing):
$\alpha_s = 0.94$, $\epsilon = 0.10$. No significant change in optical properties observed for all test conditions.

Analytical Methods: Scanning electron microscopy, X-ray diffraction. Fine scale surface microstructure remains to be quantified.

Degradation Modes:

None observed.

Comments:

At 300 °C degradation of the adhesive occurred resulting in wrinkling of the surface foil.

Reference:

P.R. Dolley and M.G. Hutchins, "Accelerated testing of selective solar absorber surfaces: I Exploratory study of surface stability for exposure to elevated temperatures in air," *Solar Energy Materials Research Laboratory Report,* 6/87, Oxford Polytechnic, April 1987.

Reference Reporting Sheet

ID Code: J 1
Number: 2
Reporter's Name: Hutchins
Ref. Date: 1987

Coating/Substrate: Cusorb - Black Ni on copper.

Manufacturer: Inco Selective Surfaces, Birmingham, U.K.

Load: Exposure to elevated temperatures in air.

Test Procedure: Exposure in air at atmospheric temperatures of 150 °C, 200 °C and 300 °C for 1h, 10h and 100h respectively.

tl"Optical Properties (before and after testing): $\alpha_s = .94$, $\epsilon = 0.11$. No significant change in optical properties for exposure to 150 °C or 200 °C. 300 °C at 1h: $\Delta\alpha_s = -0.02$. 300 °C at 100h: $\Delta\epsilon = -0.03$, $\Delta\epsilon = +0.07$.

Analytical Methods: Scanning electron microscopy, X-ray diffraction. SEM studies revealed evidence of blistering and surface cracking at localized sites following exposure to the highest temperature. Scale of microstructure essentially unaffected although not quantified.

Degradation Modes:

Unknown.

Comments:

Upon heating to 300 °C for 100h the surface changed in appearance from an initial black color to a gold-brown.

Reference:

P.R. Dolley and M.G. Hutchins, "Accelerated testing of selective solar absorber surfaces: I Exploratory study of surface stability for exposure to elevated temperatures in air," *Solar Energy Materials Research Laboratory Report,* 6/87, Oxford Polytechnic, April 1987.

Reference Reporting Sheet

ID Code: J 7
Number: 1
Reporter's Name: Hutchins
Ref. Date: 1987

Coating/Substrate: Maxorb - black Ni foil adhered to an aluminum substrate.

Manufacturer: Inco Selective Surfaces Ltd., Birmingham, U.K.

Load: Controlled temperature-relative humidity cycling.

Test Procedure: 10 cycles of 6h at 30 °C and 9510 R.H., and 6h at 60 °C and 95% R.H. with a 6h transition for change of conditions. Total test time: 180h. Derivative test of MIL STD 810D.

Optical Properties (before and after testing):

$\alpha_s = 0.94$, $\epsilon = 0.10$. No significant change observed following test.

Analytical Methods: Secondary electron microscopy, X-ray diffraction.

Degradation Modes:

None observed.

Comments:

Further testing in progress under different conditions of temperature, relative humidity and duration.

Reference:

P.R. Dolley and M.G. Hutchins, "Accelerated testing of selective solar absorber surfaces: I Exploratory study of surface stability for exposure to elevated temperatures in air," *Solar Energy Materials Research Laboratory Report,* 6/87, Oxford Polytechnic, April 1987.

Reference Reporting Sheet

ID Code: J 7 Number: 2

Reporter's Name: Hutchins Ref. Date: 1987

Coating/Substrate: Cusorb - black Ni on copper.

Manufacturer: Inco Selective Surfaces Ltd., birmingham, U.K.

Load: Controlled temperature-relative humidity cycling.

Test Procedure: 10 cycles of 6h at 30 °C and 959 R.H.
and 6h at 60 °C and 95% R.H. with a 6h transition for change of conditions. Total test time: 180h. Derivative test of MIL STD 810D.

Optical Properties (before and after testing):
$\alpha_s = 0.94$, $\epsilon = 0.11$. No significant change observed following test.

Analytical Methods: Secondary electron microscopy, X-ray diffraction.

Degradation Modes:

None observed.

Comments:

Further testing in progress under different conditions of temperature, relative humidity and duration.

Reference:

P.R. Dolley and M.G. Hutchins, "Accelerated testing of selective solar absorber surfaces: I Exploratory study of surface stability for exposure to elevated temperatures in air," *Solar Energy Materials Research Laboratory Report,* 6/87, Oxford Polytechnic, April 1987.

APPENDIX C

THERMAL STORAGE MEDIA

APPENDIX: THERMAL STORAGE MATERIALS

Reference Reporting Sheet

ID-Code: A2
Number: 1
Reporters Name: M. Yoshikawa
Ref. Date: 1975
Material: $Na_2SO_4 \cdot 10H_2O$
Load: Cyclic temperature

Degradation Modes:

Degradation of the thermal storage capacity is caused by incongruent melt accompanied by phase separation.

Comments:

Mixture of sodium sulfate decahydrate, borax as a nucleating agent, and hydrous magnesium aluminum silicate (attapulugus clay) as a homogenizing agent was proposed as a thermal storage material. This mixture had been subjected to more than 100 heating cooling cycles without any apparent phase separation.

Reference:

M. Telkes, U.S. Patent 3,986,969 (1975).

Reference Reporting Sheet

ID-Code: A2
Number: 2
Reporters Name: M. Yoshikawa
Ref. Date: 1980, 1981
Material: Glauber's salt and borax mixture
Load: Cyclic temperature

Test Procedure:

Thermal capacity of the sample was measured by means of a standard calorimetric technique in which the heat absorbed by the sample equated to the heat loss by the calorimeter's water after appropriate corrections of heat losses.

After the calorimeter measurement, the sample is placeed in a temperature cycling chamber. The air temperature in the chamber cycles from 11 to 41 °C and the sample temperature from 27 to 38 °C. Each half cycle has 4-hr period. To minimize the loss of moisture over prolonged cycling, the samples are kept in an atmosphere saturated with water vapor.

Degradation Modes:

Pure Glauber's salt melts incongruently because the anhydrous Na_2SO_4 is insoluble in the water of crystallization released during melting. Consequently, a part of Na_2SO_4 (about 15%) is precipitated. And by melting-freezing cycle the crystals of Na_2SO_4 grow gradually. The phase separation and the growth of the Na_{SO_4} crystals cause the degradation of thermal storage performance.

Comments:

Mixture of Glauber's salt and borax thickened with attapulgite clay shows a significant improvement in performance as a function of thermal cycling compared to the unthickened mixture.

Reference:

S. Marks, Solar Energy 25 (1980) 255. S. Marks, 15th IECEC 259 (1980). S. Marks, U.S. Patent 4,349,446 (1981).

Reference Reporting Sheet

ID-Code: A2
Reporters Name: M. Yoshikawa
Material: $Na_2SO_4 \cdot 10H_2O$
Load: Cyclic temperature

Number: 3
Ref. Date: 1982

Test Procedure:

Glauber's salt in a rolling cylinder was subjected to melt-freeze cycles at the rate of one cycle per day. The cylinder rotation rate was about 3 rpm. The cylinder was subjected to rate calorimetry periodically, usually once every ten cycles.

Degradation Modes:

Degradation is caused by incongruent phase transition accompanied by phase separation.

Comments:

Glauber's salt had been melt-freeze cycled 200 times in a rolling cylinder with 100% recovery of the theoretical latent heat and without performance degradation.

Reference:

C.S. Herrick, Solar Energy 28 (1982) 99.

Reference Reporting Sheet

ID-Code: A2
Reporters Name: M. Yoshikawa
Material: $Na_2SO_4 \cdot 10H_2O$
Load: Cyclic temperature

Number: 4
Ref. Date: 1984

Test Procedure:

Mixture of sodium sulfate (Na_2SO_4), water and borax was held in the test tube rotating at the rate of 5 rpm and was applied heating and cooling cycle in water chamber.

Degradation Modes:

Degradation is caused by incongruent melt accompanied by phase separation, and by growth of precipitated crystals of unhydrous Na_2SO_4 during the melting and freezing cycle.

Comments:

Rotational system will help to minimize gravity effects with Glauber's salt, while a mixture of Glauber's salt with 0.95% dry highly pulverized agricultural borax seems to minimize supercooling effects with the PCM.

Reference:

C. Onwubiko, L.D. Russel, Solar Energy 33 (1984)465.

Reference Reporting Sheet

ID-Code: A2 Number: 5
Reporters Name: M. Yoshikawa Ref. Date: 1984
Material: $Na_2SO_4 \cdot 10H_2O$–$Na_2CO_3 \cdot 10H_2O$ Mixture
$Na_2SO_4 \cdot 10H_2O$–$CO(NH_2)_2$ Mixture
Load: Cyclic temperature

Test Procedure:

Sample was in the package made of polyethylene film laminated by aluminum, and was applied to heat cycles of melting and freezing. 3 to 4 cycles were carried out in a day.

Analytical Modes:

Heat of fusion was measured by DSC and by a insulated calorimeter.

Degradation Modes:

Degradation is caused by incongruent melt accompanied by phase separation, and by growth of precipitated crystals of anhydrous Na_2SO_4 during melting and freezing cycle.

Comments:

Crosslinked acrylic acid polymer was found as an appropriate thickner which prevents the mixture from phase separation and growth of Na_2SO_4 crystal.

Reference:

T. Takeda, Y. Kudoh, Y. Machida, Journal of Energy and Resources 5 (1984)484. (in Japanese).

Reference Reporting Sheet

ID-Code: A2 Number: 6
Reporters Name: M. Yoshikawa Ref. Date: 1985
Material: $Na_2SO_4 \cdot 10H_2O$
Load: Cyclic temperature

Analytical Methods:

The operational efficiency of PCM when it is used as a thermal storage, and its mathematical description were examined.

The thermal efficiency of a thermal storage system during its (n+1)st temperature cycle, usually diurnal, will be determined by the cumulative deterioration that has taken place during the preceeding n temperature cycles.

Degradation Modes:

Deterioration is caused by the precipation from the solution during the cooling part of each cycle of a certain fraction of the salt in anhydrous crystalline form.

Comments:

The mathematical quantification of the rate of gradual decrease of this efficiency over time would be a principal guide in the determination of the useful economic life of PCM thermal storage system.

Reference:

S.C. Lowell, S.C. Saunders, PB Rep. (PB-86-105699) 1985.

Reference Reporting Sheet

ID-Code: A2
Reporters Name: M. Yoshikawa
Material: $Na_2SO_4 \cdot 10H_2$
Load: Cyclic temperature

Number: 7
Ref. Date: 1986

Test Procedure:

A new storage type, called GLS, was developed, in which the heat is transferred in a closed container to the latent heat storage material by means of the vapour of a heat transfer liquid. Glauber's salt was used for investigations in the GLS storage unit. Ethyl bromide was used as the heat transfer liquid. An alkyl sulphate was used as a surface-active substance. And one percent borax as a nucleating agent was added to the GLS storage unit.

Degradation Modes:

Degradation is caused by incongruent phase transition accompanied by phase separation.

Comments:

The investigations which were carried out in the laboratory and pilot apparatus have shown no decrease in the storable energy over the test period of 5 months. The Na_2SO_4 which was formed after melting of the Glauber's salt has a microcrystalline structure and is completely rehydrated in the course of the discharge process.

Reference:

H.H. Emons, R. Naumann, W. Voigt, Int. J. Energy Research 10 (1986) 69.

Reference Reporting Sheet

ID-Code: A2,B-2
Reporters Name: M. Yoshikawa
Material:
$Na_2SO_4 \cdot 10H_2O$, $CaCl_2 \cdot 6H_2O$
Load: Cyclic temperature

Number: 8
Ref. Date: 1984

Analytical Methods:

Thermodynamic characteristics were proposed to enable descriptions for deterioration of hydrated salt. These are related in an equation of state for triads of characteristics so that any one of them can be calculated if the other two are known.

Degradation Modes:

Deterioration is caused by incongruent phase transitions accompanied by phase separation.

Comments:

Predictions deduced from state equations are tested experimentally with systems undergoing rapid (or purely incongruent) and slow (or pseudocongruent) phase transition ($CaCl_2 \cdot 6H_2O$ and $Na_2SO_4 \cdot 10H_2O$, respectively). Good accordance between prognosis and experiment is known.

Reference:

Z. Stunic, Solar Energy 33 (1984) 593.

Reference Reporting Sheet

ID-Code: B2 Number: 9
Reporters Name: M. Yoshikawa Ref. Date: 1987
Material: $CaCl_2 \cdot 6H_2O$
Load: Cyclic temperature

Test Procedure:

An inner vessel which held the material to be tested was kept in Dewar flask containing a weighed amount of water. The water was stirred by mechanical stirrer through the center. Temperatures of the material and the water were measured by thermocouples.

Analytical Methods:

The heat of melting was measured by calorimetric methods.

Degradation Modes:

Degradation of $CaCl_2 \cdot 6H_2O$ is due to stratification caused by the formation of tetrahydrate.

Comments:

Stratification can be enhanced by cooling exceedingly slowly while passing through the crystallization zone.

Reference:

H. Feilchenfeld, J. Fuchs, S. Sarig, Solar Energy 32 (1984) 779.

Reference Reporting Sheet

ID-Code: B2 Number: 10
Reporters Name: M. Yoshikawa Ref. Dates: 1984-1985
Material: $CaCl_2 \cdot 6H_2O$ and $CaCl_2 \cdot 6H_2O$ mixtures
Load: Cyclic temperature

Test Procedure:

Samples were sealed in a 950 mm-long glass tube of 18 mm inside diameter with rubber plugs. Sample height in the molten state was about 900 mm. The tubes were held vertically in a bigger tube of 100 mm inside diameter, through which water was circulated with a pump for thermal cycling between 18 and 35 °C. Heating and cooling rates were 14 and 23 °C/hr., respectively. The samples were kept at 35 °C for 60 minutes to ensure complete melting, while no keeping time was provided at 18 °C. One cycle requires 3 hrs.

Analytical Methods:

Heat of fusion: DSC
Temperature of samples in heat cycling: TC

Degradation Modes:

Pure hydrate exhibits phase separation caused by the formation of $CaCl_2 \cdot 4H_2O$ during repeated freeze-thaw cycling.

To suppress the phase separation, addition of agents such as barium salts, excess water, and sodium chloride is proposed.

Comments:

Durability for heat cycles over 1000 times was obtained by addition of appropriate agents such as NaCl.

Reference:

H. Kimura, J. Kai, Journal of Energy and Resources 5 (1984) 586. (In Japanese).
H. Kimura, J. Kai, I. Karino, ibid. 6 (1985) 528. (In Japanese).
H. Kimura, J. Kai, Solar Energy 33 (1984) 49.

Reference Reporting Sheet

ID-Code: C2 Number: 11
Reporters Name: M. Yoshikawa Ref. Date: 1987
Material: Pentaerythritol
Manufacturer: Katayama Kagaku Kogyo Co. Ltd.
Load: Cyclic Temperature

Test Procedure:

About 5 grams of pentaerythritol in a pilex test tube was exposed to a two-month heating-cooling cycle which simulated the daily insulation: 8-hour holding at 200° C as the highest temperature in a day followed by 5-hour holding at 30° C as the lowest.

Analytical Methods:

The following physical and chemical properties were measured. Heat of transition and transition temperature by DSC Element analysis, temperature dependence of heat decomposition by TGA-DTA, and Chemical structure: NMR, IR.

Degradation Modes:

Several changes in pentaerythritol e.g. weight decrease, decrease in oxygen content, production of carbonyl compounds, and lowering of the heat of transition and of the transition temperature are thought to be caused by sublimation, thermal oxidative decomposition and crosslinking between radicals produced.

Comments:

Radical scavengers effectively suppressed the thermal degradaton of pentaerythritol. To use pentaerythritol as thermal storage material, the suppresion of sublimation, of oxidation and of radical production are required.

Reference:

H. Taoda and K. Hayakawa, Kagaku Kogaku Ronbunshu 13 (1987) 51 (in Japanese).

Reference Reporting Sheet

ID-Code: D1 Number: 12
Reporters Name: M. Yoshikawa Ref. Date: 1984
Material: Pentaerythritol
Manufacturer: Koei Chemical Co.
Load: Constant temperature in contact with some heat transfer fluids

Test Procedure:

Pentaerythritol powder was placed in a sealed glass container, which can be used for DSC measurement, both with and without the heat transfer fluids in a nitrogen atmosphere from which oxygen was exclusively purged. The glass container was maintained in the temperature range 195-200 °C, i.e., in the charging state, for long durations up to 1000 h.

Analytical Methods:

The DSC measurements were made intermittently for these samples to observe the behavior of transition.

Comments:

Pentaerythritol is useful in the temperature range 150-200 °C, and the compatibility with heat transfer fluid of hydrocarbon, such as askyldiphenylethan, alkydiphenyl and Caloria HT, was found to be very good.

Reference:

R. Sakamoto, M. Kamimoto, Y. Takahashi, Y. Abe, K Kanari, T. Ozawa, Thermochimica Acta. 77 (1984) 241.

Reference Reporting Sheet

ID-Code: D2
Reporters Name: M. Yoshikawa
Material: Polyethlyene
Load: Cyclic temperature

Number: 13
Ref. Dates: 1983, 1985

Test Procedure:

About 3 grams of sample polyehtylene pellets in a pilex test tube were exposed to over 6 months heating-cooling cycle which simulates the following daily insulation: 8-hour holding at 150 °C, and 5-hour holding at 30 °C in a day.

Analytical Methods:

Element analysis. Heat of crystallization and crystallization temperature by DSC Molecular weight etc. by fast liquid chromatography Temperature; dependence of heat decomposition by TGA-DTA; Identification of product gas by gas chromotography.

Degradation Modes:

The lowering of heat of crystallization and of crystallization temperature are thought to be caused by both the decrease in molecular weight of PE due to thermal oxidative decomposition and the crosslinking between produced radicals.

Comments:

By this study it was demonstrated that PE pellets can endure long periods of practical heat-cycling, if they are treated with radical scavengers and if the degree of crosslinking is properly controlled.

Reference:

H. Taoda, K. Hayakawa, K. Kawase, M. Kosaka, Kobunshi-Ronbunshu 42 (1985) 151; Reports of Govt. Ind. Res. Inot., Nagoya 32 (1983) 237; ibid. 34 (1985) 49 (in Japanese).