LOW TEMPERATURE DEPOSITION TECHNIQUES FOR THIN FILM
SELECTIVE SURFACES FOR SOLAR ENERGY ABSORPTION

by

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STATEMENT BY AUTHOR

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ABSTRACT

Solar energy is frequently mentioned as an alternative energy source to replace the declining supplies of fossil fuels. Photothermal conversion is especially attractive for heating and cooling purposes. The efficiency of a photothermal collector may be improved by using a selective surface to increase the energy absorbed and reduce the energy lost by radiation. It has been shown that a thin film of chromium oxide on aluminum has very desirable selective surface properties. Many techniques are available for depositing thin films on metal substrates, including evaporation, sputtering, electrochemical deposition, chemical vapor deposition, and solution spraying. From an engineering standpoint, solution spraying appears most practical. An apparatus was constructed to spray solutions of chromium compounds, particularly chromium nitrate, onto a heated aluminum substrate. Thermal decomposition during baking produced films of chromium oxide. Spray nozzle characteristics had a strong effect on the film distribution, while the substrate temperature was the most significant variable affecting film adhesion. Infrared radiation reflectance scans provided information on the chemical composition of the films and the effect of baking time on the thermal decomposition of chromium nitrate to chromium oxide. Some modification of the solution spraying technique could probably be used for commercial production of solar panels.
For a long time, the ready availability of cheap energy was taken for granted by most Americans. In recent years, however, the shortages and embargoes of fossil fuels have awakened nearly everyone to the reality that energy is a valuable commodity in short supply. As a result, many alternate energy sources are being studied, and the various methods of solar energy conversion show promise of providing a portion of the world's energy needs.

1.1 The Need for Solar Energy

At the present time, fossil fuels are the basis for the energy economy of the United States and the rest of the world. However, coal, petroleum, and natural gas must be recognized as natural resources with finite limits. Economic and political developments within the past few years have made people aware that these limits are rapidly being approached.

There have been many estimates of the fossil fuel reserves in this country. Linden (1975) has given extensive data on proven and recoverable reserves and estimates of total remaining recoverable reserves. He has also calculated how long these reserves might last, based on various conditions of energy use. For example, if the United States were self-sufficient in energy with a four percent growth rate,
the proven reserves of oil, coal, and natural gas would be down to a ten-year lifespan in 27 years, or 70 years based on the estimates of all remaining fossil fuels. It should be noted that these statistics do not consider any economic or environmental effects from this degree of development.

Nuclear fission has been widely proclaimed as the solution to our energy problems. One ton of uranium dioxide fuel is roughly equivalent to 60,000 tons of coal for the generation of electricity. However, this energy source depends on the availability of U-235, which comprises only 0.7 percent of naturally occurring uranium. As is the case with fossil fuels, uranium is a natural resource with finite limits which can be reached. Uranium reserves are generally given as tons of $\text{U}_3\text{O}_8$ available at specific costs, with production costs increasing with decreasing $\text{U}_3\text{O}_8$ concentration in the ore. Estimates of uranium reserves and cumulative requirements given by Rose (1974) indicate that cheap uranium will be used up relatively quickly. Nuclear power has recently been the subject of much public debate, with individuals and groups expressing concern over the safety of nuclear reactors and the disposal of radioactive wastes. This public awareness and rapidly increasing costs have resulted in a decrease in the number of nuclear reactors being ordered for commercial power generation.

The introduction of breeder reactors could allow the use of the 99.3 percent of natural uranium which is U-238 by converting it to fissionable Pu-239. This process would increase the potential energy available from fission by a factor of well over 100. However, this type
of reactor is not yet commercially available and, if it were, it would most likely be the object of more public opposition than is currently directed at standard reactors.

The fusion of deuterium to produce helium has the potential of producing an almost unlimited supply of energy. The fusion of the deuterium in one cubic meter of sea water could provide energy equivalent to 2,000 barrels of oil, and one cubic kilometer of sea water would be roughly equal to the world's total oil reserves (Lidsky 1972). However, fusion power is still only in the early stages of development, and tremendous engineering problems must be solved before this energy source can be made commercially available.

Geothermal energy is another alternative for electrical power generation, but it is not likely to provide more than a small fraction of our energy requirements. In hot-water geothermal systems, only about one percent of the heat may be extracted and converted to electricity with present technology (Muffler and White 1972), and only two to five percent of the heat may be recovered in the much less common vapor-dominated systems. Muffler and White have estimated that the total potential for electrical generation from geothermal wells to a depth of three kilometers is only $2 \times 10^{19}$ calories. There are currently several geothermal power generation plants around the world, the largest of which is the plant at The Geysers in California, rated at about 500 megawatts. It is not likely that geothermal energy will ever provide more than ten percent of the electrical power demand, but it may become a major source in favorable locations.
The conversion of the energy in tides may also be important in some areas. This energy is derived from the combined kinetic and potential energy of the earth, the moon, and the sun, and may be recovered by building dams to isolate basin areas from the ocean. Electric power may then be generated as the water flows into and out of the basins. The potential for power generation is fairly limited, being restricted to favorable locations, and it has been estimated to be only one percent of the total energy available from water power (Hubbert 1969). The most favorable location in North America is in the Bay of Fundy, with several possible basin areas, and a total generating potential of over 29,000 megawatts.

In contrast to the finite limits of fossil fuels and other energy sources, solar energy represents an almost inexhaustible supply of energy. The solar energy received by only 0.15 percent of the United States land area, or 4,300 square miles, is equal to the total energy consumption of \(65 \times 10^{15}\) BTU in 1970 (Williams 1974, p. 1). If this solar energy could be converted to more usable forms of energy at an efficiency of ten percent, then the nation's energy requirements could be supplied by collectors covering 1.5 percent of the land area. Even allowing for increased consumption, four percent of the land area could provide the energy needs of the year 2000. This supply of energy depends only on the sun continuing to shine, and it cannot be controlled by a foreign embargo.
1.2 Methods of Solar Energy Conversion

There are a number of processes available or proposed for the conversion of solar energy to electrical or thermal energy. The most useful direct methods are photovoltaic conversion and photothermal conversion. The purpose of this research is primarily related to photothermal conversion, which will be discussed in greater detail in the following section.

Photovoltaic solar energy conversion makes use of the ability of some semiconductor materials to convert radiant energy directly to electrical energy. The efficiency of this conversion ranges from four to five percent for cadmium sulfide cells and up to 12 percent for silicon cells (Hottel and Howard 1971, p. 343). Photovoltaic solar cells have been widely used in the space program to provide power for satellites. Systems of this type have also been used in applications such as powering navigational lights for the Coast Guard on remote buoys, or radio repeaters located on mountain tops. The main disadvantages of photovoltaic solar energy conversion are the high costs, about $25/watt (Williams 1974, p. 54) and the difficulty of storing large quantities of electrical energy. Williams (1974, p. 57) has also projected that by 1990 a solar cell array covering 192 square miles could provide the electrical energy needs of Arizona, 14,300 MWe, at a cost of $58 billion. The system would include pumped storage and assumes a solar cell cost of $1/watt. It is also estimated that the cost of solar cells must be reduced to about $0.20/watt before they are practical for central power generation.
Several other energy conversion schemes depend indirectly on solar energy. The thermal gradient between warm ocean-surface water and cold deep water may be used for power generation. Systems of this type may use low-pressure steam, derived from warm surface water in a flash evaporator, to drive a turbine. The steam is then condensed at the lower deep-water temperature. Other working fluids with high vapor pressures, such as ammonia or butane, in similar cycles. Because the temperature difference being used is only around 20°C, these systems are limited to low thermal efficiencies of three to four percent. Demonstration plants have been built to use ocean thermal gradients, but they have not been too successful. A 22-kilowatt plant built in 1929 at Mantazas Bay, Cuba, only obtained an efficiency of one percent (Williams 1974, pp. 82-83), and was not economically competitive. The French built two 3.5-MWe plants in 1956 off the Ivory Coast. These plants used an eight-foot diameter pipe reaching a depth of three miles to have a temperature difference of 36°F. Their efforts failed due to maintenance difficulties and high power requirements to operate the plant.

A portion of the solar energy received by the earth is converted to kinetic energy in air molecules, thereby contributing to winds. It has been estimated that this kinetic energy may be as high as 1 to 1.5 percent of the solar energy, and practical wind-power systems could provide up to 10^9 kilowatt-hours per year in the United States (Heronemus 1973). Windmills have been used for a long time for pumping water or grinding grain, but electrical power generation is a relatively new idea. A 1.25-MWe wind power plant built near Rutland, Vermont, in 1939
was shut down in 1945 after a blade was broken during a storm, and an 800-KWe plant in France suffered the same fate in 1960 after 18 months of operation (Williams 1974, pp. 98-101). There are several small wind-powered generating systems with storage batteries which are available commercially and may be practical in remote locations.

Another possibility for solar energy utilization is through photosynthetic conversion. Growing plants may absorb up to three percent of the incident solar energy, which can later be recovered through a variety of processes (Williams 1974, pp. 76-81). The most direct method would be to burn plants as the fuel in a steam-cycle generating station. Another procedure could be to grow algae on sewage ponds, and use the algae to produce methane by anaerobic fermentation. This method would also aid in sewage disposal problems. It is also possible to process organic wastes, from sewage or animal feedlots, which are ultimately derived from photosynthesis, to produce gaseous, liquid, or solid fuels. The fossil fuels which presently supply most of our energy are the result of photosynthetic conversion and storage in the geologic past.

Hydroelectric power can also be considered a form of solar energy conversion. The hydrologic cycle depends on solar energy for evaporation of ocean water and winds for transportation. After this water vapor is precipitated as rain or snow at higher elevations, it may be controlled to drive hydroelectric generating plants. In 1970, the United States had 53,000 megawatts of hydroelectric generating capacity (Hubbert 1973). This amount was estimated to be 32 percent of the total
potential capacity. A limitation on the lifespan of most hydroelectric projects is that they require construction of dams and reservoirs which fill with sediments from stream erosion.

1.3 Photothermal Conversion Technology

Photothermal solar energy conversion techniques make use of collectors which absorb radiant solar energy and convert it to thermal energy. A heat transfer fluid, generally air or water, is used to carry the heat from the collector to the point where it can be used. Depending on the end use of the energy, some form of storage will usually be required. Photothermal conversion systems can be divided into two general categories, flat-plate collectors and concentrating collectors, each of which contains many variations.

Flat-plate collectors are mounted at a fixed angle with the horizontal which depends on the latitude of the installation. The heat transfer fluid could flow through pipes welded to a collector plate, or through channels between parallel plates. The energy storage system depends to some extent on the fluid being used. A hot-water tank might be best for a water system, or a bed of hot rocks for an air system. Heat may also be stored in some salts which undergo phase changes at appropriate temperatures.

Flat-plate collector systems are limited to fluid temperatures of only 190 to 200°F by the re-radiation of energy in the infrared region. However, energy in this temperature range is suitable for many applications which may presently be using and wasting higher quality forms of energy, such as natural gas and electricity. A number of
flat-plate systems are currently available for purposes such as domestic water and space heating, and swimming pool heaters are becoming fairly common. Cooling is also possible with these systems using an absorption refrigeration cycle. For flat-plate systems to have any significant effect on the overall energy situation, it will be necessary to design systems which may be installed in existing structures and are compatible with the existing heating or cooling systems. This will probably require individual designs and modifications for each installation. However, with about 24 percent of our total energy consumption being used for water and space heating and refrigeration (Fowler 1972), it would be very worthwhile from an energy standpoint to convert to solar energy. Economic evaluations, though, might show that for specific applications other energy systems may be cheaper at current fossil fuel prices.

Concentrating collectors may be used when higher temperatures are desired, with the temperature depending to some extent on the concentration ratio. A ratio of around ten may be obtained by a cylindrical mirror with a parabolic cross-section and a pipe at the focal point carrying a heat transfer fluid. Higher ratios are available in a number of proposed systems which use an array of mirrors focused at a single point. One drawback to concentrating systems is that they must have some sort of tracking mechanism to keep the collector at the focal point at the position of the sun changes.

Any proposal for electrical power generation from photothermal conversion requires some form of concentration to reach the temperatures
needed for efficient steam generation. One such proposal is the power tower concept, with an array of mirrors, covering a square mile or more, focused at a boiler mounted on a tower up to 1,500 feet tall (Williams 1974, p. 49). Optimistic estimates indicate that this system could be competitive with fossil fuel power plants, and demonstration plants are now proposed or under construction in a few locations.

1.4 Objectives of Research

The main objective of this project is to study the techniques for preparation of thin-film selective surfaces for flat-plate solar energy collectors, and to develop a procedure which may be readily scaled up for production of large solar energy panels. A literature review (Chapter 2) has revealed disadvantages with most thin-film production techniques, and has indicated that a solution spraying technique holds the most promise for mass production applications. Other researchers have determined that a black chromium oxide film on an aluminum substrate has optical properties which allow highly efficient collection of solar energy. Therefore, the primary goal of this project is to develop a solution spraying technique for the deposition of thin films of chromium oxide on aluminum substrates.

A number of experimental parameters must be considered, the first of which is the selection of solution chemicals. Chromium nitrate will decompose at a relatively low temperature to produce the desired black oxide. Other possibilities to be considered are organo-chrome compounds, such as chromium acetylaectonate, which decomposes readily to form oxides. Additional variables to be studied are the solution
concentration, the duration of the spraying, the temperature of the substrate during spraying, and the time and temperature of baking, if any, after spraying. The amount of chromium oxide deposited may be found from initial and final masses of the substrate, and comparison with the amount sprayed will give an efficiency for the spray. A possibility for improving the efficiency and for producing a more uniform coating is by the use of electrostatic precipitation of spray droplets on the substrate.

Theoretical background will include details of the optical characteristics which lead to the selective surface effect, and why the films should be a specific thickness. Also included should be calculations to determine the droplet distribution in the spray and, hence, the non-uniformity of the film across the substrate. Further calculations should allow the prediction of improved spray efficiency and greater uniformity of deposition by the use of electrostatic precipitation.

After spraying and baking, the sample plates should be inspected visually. An obviously non-uniform deposit would be unsatisfactory, and such samples need not be tested further. The effectiveness of the selective surface on satisfactory samples could be tested by using an infrared sensor to measure reflectance as a function of temperature. The results could then be correlated with experimental variables and film thicknesses. It should also be possible to compare experimental results of spray efficiency and distribution with predictions based on the theoretical model, and the test results should also correlate with the predictions based on optical theory.
CHAPTER 2

REVIEW OF THIN-FILM TECHNOLOGY

There are many references in the literature discussing techniques for deposition of thin films. A broad range of film materials and substrates is covered, and many different procedures are described. These procedures may be classified under several general methods, including evaporation, electrochemical deposition, sputtering, and chemical vapor deposition.

The evaporation technique requires vaporizing the desired film material under high vacuum and allowing it to diffuse to the cooler substrate, on which the film is condensed. Using the sputtering technique, a target cathode of the desired film material is bombarded by high-energy ions in high vacuum, and atoms or molecules are physically broken loose from the target. In this process, the particles become ionized and are driven by the electric field to the anode substrate where the film is deposited. Thin films may be deposited by electroplating at low current densities and low electrolyte concentrations. For consistent film quality the concentration, current density, and temperature should be constant across the surface being plated.

Chemical vapor deposition involves vaporizing a compound of the desired film material and transporting the vapor to a heated substrate, on which it reacts with another component of the gaseous mixture to
deposit the desired material on the substrate. A variation on this technique is to spray solutions such that they react on the substrate to produce the desired film. It is also possible to spray solutions of inorganic or organometallic compounds on a heated substrate where they undergo pyrolysis to give a film of the desired material.

Because of the great many references on these methods, the following sections will describe only a few characteristic examples of each technique.

### 2.1 Evaporation

The evaporation method has been used for making thin films of several different metals and compounds. A film of high purity copper (99.99 percent) has been deposited on a silicon wafer substrate with a coating of 1,000 a.u. of $\text{Al}_2\text{O}_3$ to ensure adhesion (Gangulee 1972). This deposition occurred at a rate of 20 a.u./sec in a vacuum of $2 \times 10^{-7}$ torr, with a substrate temperature of 300°C. A copper coating has also been produced by evaporation of copper in an oxygen atmosphere in a pressure range from $6 \times 10^{-5}$ to $1 \times 10^{-2}$ mm Hg (Herrick 1964). Highly reflective coatings have been prepared by evaporation of aluminum at a high deposition rate of 500 Å/sec to avoid contamination with oxygen (Bradford and Hass 1965). Gold films on cellulose nitrate were deposited by evaporation of gold in a nitrogen atmosphere at pressures from 0.5 to 3.0 mm Hg (Harris, McGinnies, and Siegel 1948).

Thin films of semiconductor and luminescent materials may also be prepared by evaporation. Moss (1961) described the deposition of cadmium sulfide films on a heated, transparent, conducting Pyrex
substrate, at a pressure of less than $10^{-5}$ mm Hg. Films from one to two microns in thickness were hard and adherent and free of pin holes. Other films for photovoltaic effects have been made by evaporation of cadmium telluride at 600°C and $10^{-5}$ mm Hg (Goldstein and Pensak 1959). These films were deposited at a rate of 1,000 Å/min on glass substrates at 150° to 200°C. Feldman and O’Hara (1957) studied evaporation techniques for making thin luminescent films for cathode ray tubes. Their evaporations were done at $5 \times 10^{-5}$ mm Hg at temperatures ranging from 1,050°C for zinc sulfide to 2,000°C for calcium tungstate. Post-firing temperatures varied from 650°C for calcium tungstate to 1,100°C for zinc silicate. Oxide films from evaporation have been discussed by Bradford and Hass (1965). They evaporated silicon monoxide with helical heating coils of tungsten wire in an oxygen atmosphere at $8 \times 10^{-5}$ torr. Silicon dioxide and alumina were evaporated by electron bombardment from an electron gun capable of 20 kilovolts and 240 milliamperes.

Although evaporation does produce good quality thin films, the high temperature and high vacuum requirements limit the practical application of this technique for production of large-size solar energy collector panels.

2.2 Sputtering

There are several variations on the general techniques of sputtering. In one of the simplest cases, films of zinc oxide, from 0.1 to 10 μm in thickness, have been produced by sputtering the compound in either an inert argon atmosphere or a reactive oxygen atmosphere (Rozgony and Polito 1966). Other films of zinc oxide have been prepared
by reactive sputtering of zinc (99.9 percent pure) in an atmosphere of argon and oxygen at 10⁻⁵ torr (Hada, Wasa, and Hayakawa 1971). This system also applied a D.C. magnetic field of several thousand gauss transversely to the electrodes. Copper or aluminum could be co-sputtered with the zinc oxide to vary the optical and electrical properties of the film.

Sputtering using an applied radio frequency voltage has an advantage in that it may be used to produce films of dielectric materials. Putner (1967) used this procedure for films of dielectrics such as silica, alumina, titanium dioxide, barium titanate, and zinc sulfide, as well as the metals aluminum and silver. His apparatus used voltages on the order of 2.8 kV to 3.0 kV in a magnetic field up to 100 gauss and at a pressure of 5 x 10⁻³ torr. Film deposition rates varied from 80 Å/min for barium titanate to 400 Å/min for silver.

In a general comparison of evaporation and sputtering, Varga and Bailey (1973) stated that the lower film deposition rate of sputtering was a disadvantage, but it allowed greater control of film thickness. Sputtered films showed better film density and adhesion than evaporated films and made more efficient use of material. They listed typical operating conditions as 1 to 15 x 10⁻³ torr sputtering pressure, a radio frequency power input of 50 to 600 watts, and deposition rates from 25 to 1,000 Å/min.

Because of the high power and vacuum conditions, the sputtering technique would not be too practical for large-scale production of solar panels.
2.3 Electrochemical Deposition

Electrochemical deposition has primarily been used for the plating of metals, but electrolyte solutions and deposition conditions may be widely varied. Thin films of copper have been electroplated on copper or platinum substrates at room temperature and at a current density of 10 ma/cm\(^2\) (Banerjee and Walker 1961). The solutions used were copper sulfate with sulfuric acid and/or glycine. Gangulee (1972) electroplated films of copper from an acid nitrate bath at 26°C on a substrate of vapor-deposited copper. Nickel films have also been deposited at current densities of 10 ma/cm\(^2\) from solutions with various concentrations of nickel sulfate, nickel chloride, and boric acid (Banerjee and Goswami 1959a). Very dilute solutions and high current densities had a tendency to favor outgrowth rather than lateral growth of the film. Further studies showed that the crystal structures and orientation of the films could be altered by adding sodium chloride and other impurities to the solution (Banerjee and Goswami 1959b).

Combined nickel and cobalt films with thicknesses from 0.05 to 0.5 microns have been electroplated from solutions such that the nickel-to-cobalt ratio in the film was approximately one-eighth of the ratio in solution (Tutovan and Velican 1971). The solution was prepared with fixed amounts of nickel sulfate, sodium sulfate, boric acid, sodium chloride, and saccharine, with the concentration of cobalt sulfate varied to control the cobalt content in the film. The plating was done at a current density of 5 ma/cm\(^2\), at a temperature of 300°K, and a pH of 5.
Chromium has been plated from solutions of sodium tetrachromate, with the total \( \text{CrO}_3 \) concentration between 300 and 400 g/l (Parthasaradhy and Subramanian 1968). Current densities ranged from 0.1 to 1.0 amp/cm\(^2\), and temperatures were from 12\(^\circ\) to 45\(^\circ\)C. Konishi and Tadagoshi (1973) were able to obtain good plating from low concentration solutions, containing 25 to 50 g/l of \( \text{CrO}_3 \), with other conditions similar to those for high concentration plating.

Metal oxide films have been produced by electroplating of cobalt and nickel on platinum and oxidizing in air (Kokoropoulos and Evans 1964). To make films of \( 2 \times 10^{-5} \) cm in thickness required 30 minutes of oxidation for cobalt at 1100\(^\circ\)C and five to six hours of oxidation for nickel. Similar coatings of copper oxide and cobalt oxide on polished nickel, silver, and platinum were prepared for selective surfaces for solar energy collection (Kokoropoulos, Salam, and Daniels 1959). They obtained films of copper oxide from \( 2.4 \times 10^{-5} \) to \( 4.9 \times 10^{-5} \) cm in thickness, and from \( 6.8 \times 10^{-5} \) to \( 19 \times 10^{-5} \) cm for cobalt oxide. The coatings were very stable at high temperatures. A "black chrome" coating has been deposited from a tetrachromate bath containing chromic acid, sodium hydroxide, fluosilicic acid, and sucrose, at a temperature of 20\(^\circ\)C and an optimum current density of 0.235 amps/cm\(^2\) (Sivaswamy, Gowri, and Shenoi 1974). The thickness of the coating and the composition of the black chrome were not given.

Although electroplating has been used primarily for metal coatings, its potential for making oxide films for solar energy
collection should not be ignored. However, at this time it does not appear as promising as some other techniques.

2.4 Chemical Vapor Deposition

Extensive information on chemical vapor deposition for a wide variety of elements and compounds is given by Powell, Campbell, and Gonser (1955) and Blocher and Withers (1970). Thin films of polycrystalline silicon, from one to three microns thick, have been deposited from mixtures of SiH$_4$ and H$_2$ at 600° to 750°C or from SiBr$_4$ and H$_2$ at 750° to 900°C (Cowher and Sedgwick 1972). These films were intended for use in semiconductor devices. In a similar study (Eversteyn and Put 1973), it was observed that the growth rate of polycrystalline silicon from a mixture of SiH$_4$ and H$_2$ could be decreased by adding AsH$_3$ or PH$_3$ or increased by adding B$_2$H$_6$, at deposition temperatures of 680°C. Silicon has also been deposited by reduction of ScCl$_4$ by H$_2$ at 1100°C on a magnesium oxide substrate (Elliot, Meikleham, and Kolbe 1961). Films from this process could be removed intact from the substrate.

Phosphorescent films of single crystal cadmium sulfide have been deposited by reacting cadmium vapor with hydrogen sulfide in a hydrogen atmosphere inside a quartz tube at 800° to 1000°C (Frerichs 1947). Similar techniques were described for films of cadmium selenide and cadmium telluride.

A T-shaped reactor has been used to make a complex yttrium iron garnet film (Kempter and Boegner 1972). Anhydrous YCl$_3$ and FeCl$_2$ were vaporized separately in the bottom of the T, and a carrier gas of argon and hydrogen chloride was introduced. Argon, oxygen, and water vapor
were added through the left side of the T, and the resulting reaction caused the deposition of the garnet film in the right side of the T.

A continuous reactor for the production of silicon dioxide films by oxidation of silane at 400°C has been developed by Benzing, Rosier, and East (1973). Their substrate wafers were automatically loaded and unloaded from a continuous belt, with the reaction zone being isolated by a nitrogen purge region. Deposition rates from 400 to 1600 Å/min were reported, with variations due to the silane concentration and the total gas flow. A cost of 5.81¢ per wafer was reported for a production rate of 200 two-inch wafers per hour at a deposition rate of 700 Å/min. This cost was compared with a batch process cost of 8.51¢ per wafer.

Thin films of a number of metals and oxides have been deposited by the decomposition of acetylacetonates (Viguie and Spitz 1975). Solutions of the acetylacetonates in butanol or acetylacetone were atomized to droplets in the two-to-eight micron range by a piezoelectric transducer. The deposition temperatures were such that the solutions were completely vaporized before reaching the substrate. Ferric oxide layers from 1800 to 2600 Å thick were deposited from a solution in butanol at 400° to 550°C in air. Chrome oxide films (Cr₂O₃) were deposited from a solution of chromium acetylacetonate in butanol at 520° to 560°C in an argon atmosphere.

Ryabova and Savitskaya (1968) have also prepared metal oxide films by pyrolysis of organometallic compounds. Zinc oxide films from 400 to 5000 Å thick were deposited by the thermal decomposition of zinc propionate and zinc acetylacetonate, with the propionate giving better
films. Chrome oxide (Cr$_2$O$_3$) films were deposited on a tantalum substrate at 750°C, on nickel at 650°C, and on vitreous silica at 500°C, from chromium acetylacetonate at 230°C. These depositions were carried out in an evacuated reaction vessel.

Although high quality films are possible from chemical vapor deposition techniques, the operating conditions are generally such that the procedures would be difficult to scale up for large solar energy collectors.

2.5 Solution Spraying

The solution spraying techniques for preparing thin films are similar to chemical vapor deposition, except that the reactants are in solution in aerosol sprays rather than in the vapor state. As with the other methods, this procedure has been used with a wide variety of film and substrate materials.

Copper films, 0.1 to 6.0 microns thick, have been prepared by reduction of copper salts by hydrazine using a dual nozzle atomizer at room temperature (Momyer and Levy 1967). This procedure could be used to make uniform, relatively pure films on either metallic or non-metallic substrates.

Thin films of sulfides and selenides have been deposited by spraying a single solution, containing a metal salt and thiourea or selenourea, onto a heated substrate (Chamberlin and Skarman 1966). For a cadmium sulfide film, concentrations from 0.001 to 0.5 M were used, with a substrate temperature of 400°C. Luminescent films have been produced by spraying solutions of zinc or cadmium halides, with an
activator, onto Pyrex or fused silica at temperatures from 850° to 1000°C (Kirk and Schulman 1961). A reaction occurred between the halides and the substrate to produce zinc or cadmium silicate phosphors. A similar technique, but one capable of producing a wider range of luminescent films, included the desired negative ion in the solution as a water soluble compound, such as tetraethyl orthosilicate for silicate phosphors (Gilliland and Hall 1967). The substrate temperature during spraying was maintained at 200° to 400°C, but firing temperatures after spraying ranged from 650°C for zinc tungstate to 1250°C for calcium magnesium silicate phosphors.

Spray techniques have also been used to produce a number of metal oxide films. Solomon (1962) deposited films of tin oxide from solutions of stannic tetrachloride in methanol on glass substrates heated to temperatures from 800° to 1200°F. Titanium dioxide coatings have been made by a hydrolysis reaction resulting from the mixing of streams of water vapor and tetraisopropyl titanate (Sladek and Herron 1972). Bach and Schroeder (1967) also deposited films of titanium dioxide, but they used the pyrolysis of titanic acid esters at 600°C on glass substrates. Films of yttrium oxide and rare earth oxides have been prepared with spray techniques using acetylacetonates at substrate temperatures above 400°C (Frank and Groth 1969).

Hottel and Unger (1959) studied spray techniques for making thin films of copper oxide on aluminum for selective surfaces for solar energy collectors. They used dilute solutions of copper nitrate, approximately 0.0025 molal, sprayed onto a heated aluminum substrate. A
baking period at 350°C following the spray converted the copper nitrate to copper oxide.

Many patents have been granted for apparatus and procedures for making thin films by solution spraying. Carlson (1960a) used a dual spray system to prepare a nickel coating. A nickel solution consisting of nickel sulfate, chloride, or formate was sprayed on the substrate and reduced by a simultaneously sprayed solution containing sodium hydrosulfite and sodium hypophosphite. Similarly, copper cyanide could be reduced by an alkali-metal hydrosulfite to form a copper coating (Carlson 1960b). Swanson (1964) used a system of consecutive sprays of aqueous stannous chloride, water rinse, and aqueous silver nitrate, followed by simultaneous sprays of aqueous cupric acetate and aqueous alkaline sodium hydrosulfite to form a copper coating on nonconductors.

Drummond (1943) developed an apparatus for depositing a metal film on a continuous metal strip by thermal decomposition of nickel, iron, chromium, and other carbonyls. Nack (1954) also formed metal films by decomposing metal carbonyls, but he made use of a radioactive source to ionize the carbonyl and an electrostatic field to drive the metal to the substrate.

A general method for making thin films of inorganic compounds included solution spraying at ambient conditions onto substrates heated to 200° to 400°F (Hill and Chamberlin 1964). The solutions contained a soluble compound of at least one group VI-A element and a soluble compound of at least one element selected from the elements of groups I-A,
II-B, III-A, III-B, IV-A, V-A, and VIII. Cusano and Studer (1954) described a method for making films in which a solution containing salts of zinc or cadmium was sprayed onto a substrate of glass or fused quartz in an atmosphere of hydrogen sulfide or selenide at a few millimeters of mercury pressure. A chemical reaction between the salt and the gas produced a luminescent film.

Films of tin oxide have been deposited on glass by the thermal decomposition of organotin compounds on a heated glass substrate (Menke 1973). For example, a solution of stannous trifluoroacetate in methyl ethyl ketone could be sprayed onto the glass substrate and decomposed at 1250°F. Nesteruk (1972) developed a process for coating glass with colored metal oxides by decomposition of organometallic compounds such as acetylacetonates. He improved the efficiency of the spray system by using electrostatic spray guns. Bamford (1972) also used the decomposition of organometallic compounds to produce films of metal oxides on continuous glass ribbons.

Because of the moderate temperature requirements and ambient pressure conditions, and because of the possibility of spraying large areas by continuous processes, it would appear that the solution spraying technique may have the best potential for making large, inexpensive, solar energy collectors.
CHAPTER 3

THEORETICAL BACKGROUND

The background for this project includes several areas of study. First, flat plate collectors must be examined and heat balance calculations should be carried out to look at the effects of variable properties. Second, it is useful to study radiation and how absorptance and emittance may be affected by material properties which can lead to the selective surface effect. Third, the chemistry and special properties of chromium compounds and aluminum are also important in this project. Fourth, the distribution of solution droplets in the spray is useful in studying spray efficiency. Fifth, possible improvements due to the use of electrostatics should be considered.

3.1 Flat Plate Collectors

Flat plate, solar energy collectors are suitable for uses which do not require high temperatures. Space heating and domestic water heating can be easily accomplished by flat plate collectors, and cooling using absorption refrigeration cycles is also possible.

Flat plate collectors are inherently simpler than concentrating collectors in that they require no tracking mechanism to follow the sun. These collectors may be mounted at a fixed angle with the horizontal, roughly 10° greater than the latitude of the installation. This angle
will slightly decrease the summer efficiency of the system, but will greatly increase the winter efficiency.

There are several possible designs for flat plate collectors. One possibility is a single plate with pipes for the heat transfer fluid welded on the back side. Construction of this type of collector would be fairly simple, but its efficiency is limited by a small area for heat transfer to the fluid and by the thermal conductivity of the plate material. A second type of collector could be constructed with the fluid flowing in channels between two parallel plates. Construction and material costs would be slightly higher for this design, but heat transfer to the fluid and overall efficiency should be higher.

The energy input to a flat plate collector includes both direct beam sunlight and diffuse light, so these collectors will function, although at reduced efficiencies, even on cloudy days. The solar constant, or the energy received per unit time per unit area, on a surface perpendicular to the solar radiation has been given as 1353 watts/m$^2$ (Duffy and Beckman 1974). The actual energy received will vary considerably with latitude, season, and time of day. The energy absorbed by a collector also depends on the area of the collector, the absorptivity of the surface, and the transmittance of the protective cover plates, if any. For a location in Arizona at noon, it is not unreasonable to use an input of 1000 w/m$^2$ for calculations, and of this amount, 850 w/m$^2$ might be absorbed by a collector.

There are several sources for heat loss from flat plate collectors. Heat may be lost from the front surface of a collector by
re-radiation, convection, and conduction. The latter may generally be ignored as it is much smaller than the first two. Heat losses by conduction from the back of a collector can be minimized by the use of insulation, such as polyurethane foam. The energy losses from the front surface may be significantly reduced by using one or more cover plates of glass or plastic. The cover plates are most effective in decreasing the convection losses, but radiation losses are also substantially reduced, due to the low transmission of infrared radiation through glass.

The various heat losses may be described mathematically to give an overall energy balance model for the flat plate collector. Duffy and Beckman (1974) go into detailed energy balance calculations, but only a few of the more basic relations will be given here. The simplest heat loss with which to deal is that through the back of the collector. This loss is primarily by conduction through a layer of insulation and may be calculated by the equation

\[ Q_b = \frac{k}{t} A(T_a - T_p) \]  

(3.1)

where \( Q_b \) is the heat loss rate from the back of the collector in watts, \( k \) is the thermal conductivity of the insulation in watts/meter °K, \( t \) is the thickness of the insulation in meters, \( A \) is the area of the solar panel in square meters, and \( T_a \) and \( T_p \) are ambient and plate temperatures in °K.

Convection losses are a little more difficult to handle and include convective transfer between the collector and the cover plate.
and between the cover plate and the ambient air. Natural convection between parallel plates can be described by empirical relationships between the Nusselt number and the Grashof number, with different constants depending on the angle of tilt of the collector. These relationships give the following equations for the convection heat transfer coefficient.

At a tilt angle of 0°,

$$h_{10} = 1.613 \frac{(T_p - T_c)^{0.281}}{L^{0.157}}$$  \hspace{1cm} (3.2)

At a tilt angle of 45°,

$$h_{10} = 1.14 \frac{(T_p - T_c)^{0.310}}{L^{0.070}}$$  \hspace{1cm} (3.3)

where $h_{10}$ is the heat transfer coefficient at an average temperature of 10°C in w/m² °K, $L$ is the spacing between the plates in cm, and $T_p$ and $T_c$ are the panel and cover temperatures in °K. To correct for temperatures other than 10°C, the following relation may be used,

$$\frac{h_T}{h_{10}} = 1 - 0.0018 (\bar{T} - 10)$$  \hspace{1cm} (3.4)

where $\bar{T}$ is the average temperature between the plates in °C. Convection losses from the cover plate to the ambient air are a strong function of the wind velocity. This heat transfer coefficient may be estimated by the following empirical relation,
where $h_{\text{wind}}$ is the convection heat transfer coefficient in w/m$^2$ °K and $v$ is the wind velocity in m/sec.

Energy transfer by radiation between two surfaces is given by the general equation,

$$Q_r = \frac{\sigma(T_2^4 - T_1^4)}{\frac{1}{\varepsilon_1 A_1} + \frac{1}{A_1 F_{1-2}} + \frac{1}{\varepsilon_2 A_2}}$$

where $Q_r$ is the radiant heat transfer rate in watts; $\sigma$ is the Stefan-Boltzmann constant, $5.6697 \times 10^{-8}$ w/m$^2$ °K$^4$; $\varepsilon$ is a dimensionless emissivity; $A$ is area in square meters; and $T$ is temperature in °K. The subscripts 1 and 2 refer to the two surfaces, and $F_{1-2}$ is a shape factor relating the surfaces. For radiation between a collector and a cover plate, $A_1 = A_2 = A$, and $F_{1-2} = 1$, so this equation reduces to

$$\frac{Q_r}{A} = \frac{\sigma(T_c^4 - T_p^4)}{\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1}$$

To express in a more standard form, a radiant heat transfer coefficient, $h_{r, p-c}$, may be defined as

$$h_{r, p-c} = \frac{\sigma(T_c^2 + T_p^2)(T_c + T_p)}{\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} - 1}$$
For radiation from the cover plate to the sky, equation 3.6 can again be simplified. This process is essentially one of radiation between a small plate and a large hemisphere, so \( A_1/A_2 \approx 0 \). The shape factor, \( F_{1-2} \), is again 1, the sky emittance, \( \varepsilon_s \), is approximately 1, and the equation reduces to

\[
Q_T = \frac{\sigma(T_s^4 - T_c^4)}{A} = A\varepsilon_1 \sigma(T_s^4 - T_c^4)
\]

Again, a general heat transfer coefficient may be defined as

\[
h_{T,c-a} = \varepsilon_1 \sigma \frac{(T_s^4 - T_c^4)}{(T_a - T_c)}
\]  

(3.10)

An empirical relation between the effective sky temperature, \( T_s \), and the ambient temperature, \( T_a \), is given by

\[
T_s = 0.055 (T_a)^{1.5}
\]

(3.11)

These various heat transfer coefficients may be combined to give an overall transfer coefficient for heat losses.

To illustrate the effects of these heat losses on the useful energy available from a solar energy collector, a sample problem will be considered, using typical values for material properties. The system will include a collector, tilted at an angle of 35° to the horizontal, with dimensions of 1.0 m by 2.0 m. A glass cover plate will be used
with overall transmittance $\tau = 0.9$ and overall emittance $\varepsilon_c = 0.88$. The collector panel and cover plate are separated by 2.5 cm, and the back is insulated with 5.0 cm of urethane foam, $k = 3.29 \times 10^{-2}$ W/m$^2$ K. An ambient temperature of $25^\circ$C and an average plate temperature of $100^\circ$C will be assumed. To illustrate the effect of a selective surface, two cases will be considered. First, the collector will be an anodized aluminum, $\alpha = 0.95$, and $\varepsilon_p = 0.95$. The second collector will have a highly selective surface, $\alpha = 0.95$, $\varepsilon_p = 0.05$. For both cases, a solar insolation of 1000 W/m$^2$ will be assumed. Details of the calculations may be found in Appendix B. For the non-selective surface, 402 watts of useful energy are available with an overall efficiency of 20.1%. The use of the selective surface makes 1037 watts of useful energy available, with an overall efficiency of 51.8%.

### 3.2 Optical Characteristics of Thin Films

It has been shown that the overall performance of a solar energy collector is strongly dependent on the optical properties of its surface. Of particular significance are the absorptance, $\alpha$, the emittance, $\varepsilon$, and the reflectance, $\rho$. Each of these properties are in turn functions of the wavelength of radiation, and values for a specific wavelength are designated by using a subscript, $\lambda$.

These properties may be related by a few simple equations. If there is no transmission of energy, the sum of the absorptance and the reflectance must equal one,

$$\alpha_\lambda + \rho_\lambda = 1 \quad (3.12)$$
Kirchhoff's law states that the absorptance and emittance are equal at any given wavelength,

$$\alpha_\lambda = \varepsilon_\lambda \quad (3.13)$$

These relationships can be combined to show that

$$\varepsilon_\lambda = 1 - \rho_\lambda \quad (3.14)$$

The wavelength distribution produced in black body radiation is a function of the temperature of the radiating body. The sun, essentially acting as a black body at 6000°K, produces radiation primarily in the range of visible light. Solar energy collectors, operating at much lower temperatures, emit primarily in the infrared region, as illustrated in Figure 3.1 (Seraphin and Wells 1973). It can be easily seen that an efficient solar energy collector should have a high absorptance in the visible range, to collect all available solar radiation, and a low emittance in the infrared region, to minimize re-radiation losses. Because these losses vary with the fourth power of absolute temperature, the emittance may become a limiting factor at higher collector temperatures. The desirable properties of a solar energy collector are illustrated in Figure 3.2 (Seraphin and Wells 1973). Another method used to describe this effect is the selectivity factor, which is the ratio of absorptance to emittance. The overall efficiency of a solar energy collector may be improved by increasing its absorptance or selectivity factor, as shown in Figure 3.3.
Figure 3.1 Solar and Blackbody Radiation Spectra.

Figure 3.2 Desirable Properties of Flat Plate Collectors.
Figure 3.3 Theoretical Thermal Efficiencies of Flat Plate Collectors. -- Efficiencies plotted as functions of absorptance and selectivity.
The reflectance from a surface may be calculated by use of the Fresnel reflection formulas (Stone 1963, p. 397),

\[
\begin{align*}
r_{\pi} &= \frac{n_1 \cos \phi - n_2 \cos \theta}{n_1 \cos \phi + n_2 \cos \theta} \\
r_{\sigma} &= \frac{n_1 \cos \theta - n_2 \cos \phi}{n_1 \cos \theta + n_2 \cos \phi}
\end{align*}
\]  

(3.15) (3.16)

where \( r_{\pi} \) and \( r_{\sigma} \) are reflection coefficients for light polarized parallel and perpendicular to the plane of incidence, \( n_1 \) and \( n_2 \) are indices of refraction for the two media, and \( \phi \) and \( \theta \) are incident and refracted angles. For normal incidence, \( \cos \phi = \cos \theta = 1 \), and the equations reduce to

\[
r = \frac{n_1 - n_2}{n_1 + n_2}
\]

(3.17)

The reflectance is given by

\[
R = r^2 = \left( \frac{n_1 - n_2}{n_1 + n_2} \right)^2
\]

(3.18)

where \( R \) is equivalent to the monochromatic reflectance, \( \rho_\lambda \).

The use of thin-film coating materials in solar energy collectors gives more complicated relationships for the reflection coefficients and reflectance. For the case of a transparent thin film on a transparent substrate, such as a coated glass cover plate for a solar
energy collector, a combined reflection coefficient for normal incidence
is given by Stone (1963, p. 414),

\[
r_{12} = \frac{(n_1 - n_2)n_f \cos \delta_1 - i(n_1 n_2 - n_f^2) \sin \delta_1}{(n_1 + n_2)n_f \cos \delta_1 - i(n_1 n_2 + n_f^2) \sin \delta_1}
\]  (3.19)

where \(n_1\), \(n_2\), and \(n_f\) are indices of refraction for air, the substrate,
and the film, respectively, and \(\delta_1\) is defined by

\[
\delta_1 = \frac{2\pi n_f d_f}{\lambda_0}
\]  (3.20)

where \(d_f\) is the film thickness and \(\lambda_0\) is the wavelength of incident
light. If materials can be chosen such that \(n_f^2 = n_1 n_2\), the reflection
coefficient becomes a cosine function which will give zero reflectance
at a film thickness of \(d_f = \lambda_0/4n_f\). These results can be used to improve
overall collector efficiency by minimizing the losses due to reflection
from the cover plate.

The net reflectance from a thin-film coating on a collector
panel can also be given at (Brannon and Goldstein 1970),

\[
R = \frac{r_1^2 + 2r_1 r_2 \cos 2\delta_1 + r_2^2}{1 + 2r_1 r_2 \cos 2\delta_1 + r_1^2 r_2^2}
\]  (3.21)

where \(r_1\) and \(r_2\) are the reflection coefficients for the air-film and
film-substrate interfaces, defined by the Fresnel relations. Defining \(R\)
in terms of indices of refraction leads to the equation,
For the case of an absorbing film on an absorbing substrate, the complex indices of refraction, \( n = n - ik \), must be used. The net reflectance is then,

\[
R = \frac{(g_1^2 + h_1^2) e^{2\mu_1} + (g_2^2 + h_2^2) e^{-2\mu_1} + A \cos 2\gamma_1 + B \sin 2\gamma_1}{e^{2\mu_1} + (g_1^2 + h_1^2)(g_2^2 + h_2^2) e^{-2\mu_1} + E \cos 2\gamma_1 + D \sin 2\gamma_1}
\]

(3.23)

with substitute variables defined as follows,

\[
g_1 = \frac{n_1^2 - n_f^2 - k_f^2}{(n_1 + n_f)^2 - k_f^2}
\]

(3.24)

\[
g_2 = \frac{n_f^2 - n_2^2 - k_f^2 - k_2^2}{(n_f + n_2)^2 + (k_f + k_2)^2}
\]

(3.25)

\[
h_1 = \frac{2n_1k_f}{(n_1 + n_f)^2 + k_f^2}
\]

(3.26)

\[
h_2 = \frac{2(n_fk_2 - n_2k_f)}{(n_f + n_2)^2 + (k_f + k_2)^2}
\]

(3.27)
\[ \mu_1 = \frac{2\pi k_f d_f}{\lambda} \]  
\[ \gamma_1 = \frac{2\pi n_f d_f}{\lambda} \]  
\[ A = 2(g_1 g_2 + h_1 h_2) \]  
\[ B = 2(g_1 h_2 - g_2 h_1) \]  
\[ D = 2(g_1 h_2 + g_2 h_1) \]  
\[ E = 2(g_1 g_2 - h_1 h_2) \]

If the optical properties of the film and substrate are known as functions of wavelength, the reflectance of a solar panel may be calculated and the effect of a selective surface may be examined quantitatively.

### 3.3 Materials for Selective Surfaces

As pointed out in the previous section, it would be desirable for a solar energy collector to be highly absorbing in the visible range of wavelengths and highly reflecting in the infrared range. Unfortunately, no single material possesses this combination of properties, so multiple-layer surfaces have been developed such that the combined effect approximates that illustrated in Figure 3.2.

The materials used in a selective surface should include a substrate which is highly reflective in the infrared region and an upper
layer which is highly absorbing in the visible range, but transparent in the infrared. Pure metals, such as gold, silver, or aluminum are among the best infrared reflectors. Semiconductor materials, such as silicon and germanium have been popular as absorbers because their properties and methods of preparation are well-known from solid-state electronics and photoelectric technology (Edwards et al. 1962). Some transition metal oxides have been shown to be good absorbers. The choice of materials can lead to complicated, multi-layered solar panels (Seraphin and Wells 1973). Some semiconductor materials require an additional outer anti-reflection coating to improve their absorptance. If the absorber and reflector might interact chemically, an inert layer must be included between them. A reflector such as gold or silver would probably be used as a thin-film metallic coating on a substrate which would serve structural and heat transfer functions.

The Department of Optical Sciences of The University of Arizona has found that a thin layer of chromium oxide deposited by chemical vapor deposition on an aluminum substrate gives a highly efficient selective surface while requiring only a single thin-film layer. As stated earlier, the purpose of this research is to investigate methods of developing similar quality films of chromium oxide on aluminum under more economical processing conditions, including ambient pressure and moderate temperatures.

Aluminum makes an excellent material for a solar collector substrate, having a total emissivity for a moderately polished surface of only 0.028 at 100°C (Weast 1967, p. E-163). This value compares
favorably with values of 0.02 for both gold and silver at 100°C. The cost of aluminum is sufficiently low to allow its use as an economical construction material for solar panels. Furthermore, its thermal conductivity is high enough to provide efficient heat transfer.

One potential problem that should be considered is the effect of a layer of aluminum oxide which will form on the surface of the substrate prior to the spray deposition of chromium oxide. Inherently, by normal exposure to the atmosphere, this film may attain a thickness of 15 Å within one hour and it may reach a final thickness of 30 to 40 Å (Bradford and Hass 1965). The effect of this film on the reflectance may be calculated using equations 3.23 through 3.33 and optical constants given by Brannon and Goldstein (1970) for aluminum and aluminum oxide in the infrared range. Results of these calculations (see Appendix C) indicate that the oxide film has practically no effect at 2.0 μ and 5.0 μ, as it is transparent at those wavelengths, and the film might decrease the reflectance by 0.07 percent at 10.0 μ. These results indicate that it is safe to neglect the oxide film when considering the overall optical properties of the collector.

Chromium oxide (Cr₂O₃), which appears black in visible light, is an effective absorber of solar energy, and being transparent to infrared radiation, it allows the substrate reflectance to minimize radiation losses. Films have been prepared in the Department of Optical Sciences by vaporization of chromium in a high vacuum. The chromium vapor reacts with residual oxygen in the apparatus to give the desired oxide coating on aluminum substrates.
Very little data are available for the optical properties of chromium oxide as functions of wavelength. Hahn (1976) has measured the index of refraction and extinction coefficient at several wavelengths between 0.55 \( \mu \text{m} \) and 2.4 \( \mu \text{m} \) for reactively evaporated chromium oxide films, but no data could be found for longer or shorter wavelengths. Using data points for chromium oxide (Hahn 1976, Figure 6.7) and similar data for aluminum at corresponding wavelengths (Hellwege and Hellwege 1962), the reflectance of a selective surface may be calculated using the equations of Section 3.2. The dependence of the reflectance on film thickness is illustrated in Figure 3.4 for wavelengths in the visible and near-infrared regions. Figure 3.5 uses the same data, but the reflectance is plotted as a function of wavelength for several film thicknesses. The data used in plotting these curves are summarized in Table C-2 (Appendix C).

Chromium oxide may be prepared by the thermal decomposition of various chromium compounds. For example, chromium nitrate can be decomposed by heating to about 400°C by the following reaction:

\[
2\text{Cr(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_3 + 6\text{NO}_2 + 18\text{H}_2\text{O} + 1 {1 \over 2} \text{O}_2
\]

This reaction might be used to prepare a coating of the oxide by spraying a nitrate solution onto a heated substrate. The progress of this reaction as a function of temperature has been studied by Vander Wall (1962) and is illustrated in Figure 3.6. The final product of decomposition is crystalline chromium oxide (\( \text{Cr}_2\text{O}_3 \)), but an amorphous
Figure 3.4 Calculated Reflectance for a Chromium Oxide-Aluminum Selective Surface as a Function of Film Thickness.
Figure 3.5 Calculated Reflectance for a Chromium Oxide-Aluminum Selective Surface as a Function of Wavelength.
Figure 3.6 Thermal Decomposition of Cr(NO₃)₃·9H₂O. -- a. Heating rate = 2.6 °C/min; weight loss = 81.2%. b. Heating rate = 1.0 °C/min; weight loss = 81.1%.
intermediate product, with the empirical formula \( \text{CrO}_{2.2} \), exists between 270°C and 390°C.

A number of oxides of chromium may exist, depending on the valence state of chromium and the conditions of preparation. Chromous oxide (\( \text{CrO} \)) may be produced by oxidation of a chromium amalgam in air or nitric acid. It is a black powder which will inflame when heated in air (Udy 1956). Chromium trioxide (\( \text{CrO}_3 \)) exists as dark-red crystals which are strongly hygroscopic. It will decompose, releasing oxygen, at temperatures estimated between 200° and 550°C. The reaction is probably incomplete in the lower part of this range. Chromium oxide (\( \text{Cr}_2\text{O}_3 \)) is the most stable of the oxides of chromium and may be produced by direct oxidation of finely divided chromium or by thermal decomposition of a number of chromium compounds.

Several intermediate oxides can exist as combinations of the three basic oxides. For example, hydrous forms of \( \text{Cr}_3\text{O}_4 \) (\( \text{CrO}\cdot\text{Cr}_2\text{O}_3 \)) have been formed by the decomposition of chromous potassium carbonate with water. It may be converted to \( \text{Cr}_2\text{O}_3 \) by the action of water vapor, hydrogen chloride, or even in an inert gas at 250°C. Chromium dioxide, \( \text{CrO}_2 \) (\( \text{CrO}_3\cdot\text{Cr}_2\text{O}_3 \)), may be formed by several reactions, including the heating of \( \text{Cr}_2\text{O}_3 \) in air, but further heating at 300°C will convert it back to \( \text{Cr}_2\text{O}_3 \). Several more complex oxides have also been reported, but these convert to \( \text{Cr}_2\text{O}_3 \) by heating.

Because of the unavoidable layer of oxide on the aluminum substrate, the bonding of the selective surface must be between the chromium and aluminum oxides. Both of these oxides have hexagonal crystal forms,
but there is some difference in their cation radii, with \( \text{Al}^{3+} \) at 0.51 \( \text{Å} \) and \( \text{Cr}^{3+} \) at 0.63 \( \text{Å} \) (Weast 1967, p. F-143). However, chromium oxide is isomorphous with aluminum oxide and their unit cell dimensions are quite close, with \( a = 4.950 \text{ Å} \) and \( c = 6.806 \text{ Å} \) for chromium oxide (Mellor 1923, Vol. 8, p. 178), and \( a = 4.86 \text{ Å} \) and \( c = 6.62 \text{ Å} \) for alumina (Mellor 1923, Vol. 5, p. 204). Thus, the deposition of the desired chromium oxide thin film may fortuitously be compatible with the inherent layer of aluminum oxide on the metallic aluminum substrate!

Thus, one possible mechanism for adhesion of the thin film selective surface is the diffusion of chromium oxide into aluminum oxide. Because of isomorphous crystal structures, this process would primarily be one of replacement of aluminum ions with chromium ions. No data have been found on the diffusivity of this specific process, but an order of magnitude estimate may be obtained by using data given by Askill (1970) for the diffusivity of rion into aluminum oxide. This reaction has an activation energy, \( Q \), of 82.0 kcal/mole and a frequency factor, \( D_0 \), of 1.13 \( \text{cm}^2/\text{sec} \). The temperature dependence of diffusivity is given by

\[
D_T = D_0 e^{-Q/RT} \tag{3.34}
\]

where \( R \) is the universal gas constant. The general equation for diffusion is

\[
\frac{dc}{dt} = D_T \frac{d^2c}{dx^2} \tag{3.35}
\]
where \( c \) is the concentration of the diffusion species as a function of time and position. For the diffusion of a thin layer into a semi-infinite medium, the solution to this equation is

\[
c(x) = c(o) \exp\left(-\frac{x^2}{4D_T t}\right)
\]

(3.36)

To apply this solution to the diffusion of chromium oxide into aluminum oxide, several cases may be considered. First, assuming a chromium oxide mole fraction of 0.001 at a distance of 10 Å (10\(^{-7}\) cm) from the interface, and solving, gives the product \( D_T t = 3.619 \times 10^{-16} \) cm\(^2\). Allowing a diffusion time of 10,000 sec gives \( D_T = 3.619 \times 10^{-20} \) cm\(^2/\)sec. Substituting into equation 3.34 and solving gives \( T = 649^\circ C \). However, since this temperature is very close to the melting point of aluminum, it would not be a suitable baking temperature for this process.

Assuming a more reasonable baking temperature of 450\(^\circ\)C, the equations may be solved to find that the time required to reach the stated concentration level is \( 2.412 \times 10^7 \) sec or 76.42 yrs. Obviously, this time period is unreasonable for either an experimental or a commercial procedure.

Again assuming a temperature of 450\(^\circ\)C and a time period of 10,000 sec, the distance from the interface at which a chromium oxide mole fraction of 0.0001 is reached may be calculated to be \( 2.34 \times 10^{-10} \) cm or 0.0235 Å. Allowing a diffusion period of 100,000 sec only increases this distance to \( 5.44 \times 10^{-10} \) cm. As these distances are an order of magnitude less than the ionic radius of chromium (Cr\(^{3+}\)), they would appear to have little physical significance.
Finally, assuming a temperature of 450°C and a time of 100,000 sec, the concentration at a depth of $10^{-8}$ cm may be calculated, with the result that $c(x) = 0.000$. From these rough calculations, it would appear that diffusion of chromium oxide into aluminum oxide is unlikely to play a significant role in the adhesion of the film to the substrate.

The thermal expansion characteristics of chromium oxide, aluminum oxide, and aluminum will influence the adhesion and durability of the thin-film coating. Udy (1956) gives data for the thermal expansion of $\text{Cr}_2\text{O}_3$ as a function of temperature with a reference point at 100°C. Heating from 100° to 200°C will give 0.07% linear expansion. There will be 0.14% expansion from 100° to 300°C, and 0.21% expansion from 100° to 400°C. Data for aluminum and aluminum oxide are available with reference points at 293°K or 20°C (Kirby, Hahn, and Rothrock 1972). Converting to a reference point of 100°C, aluminum oxide will have 0.074% linear expansion from 100° to 200°C, 0.156% expansion from 100° to 300°C, and 0.243% expansion from 100° to 400°C. The data for aluminum give linear expansions of 0.255% from 100° to 200°C, 0.524% from 100° to 300°C, and 0.816% from 100° to 400°C. The difference in thermal expansion between $\text{Cr}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$ might act to relieve internal stresses caused by differences in crystal dimensions. The thin layer of $\text{Al}_2\text{O}_3$ should also help relieve the stresses due to the large differences in thermal expansion between the chromium oxide film and the aluminum substrate.
3.4 Spray Distribution

The utilization of finely dispersed liquid droplets by means of an atomizing spray is attractive from an engineering standpoint, but it does present a problem of uniform distribution of material on the substrate surface. This problem of the coating distribution may be approached by first considering the distribution of solution droplets in the spray. This distribution may be discussed in terms of a droplet flux density, \( N \), in droplets per unit time per unit area perpendicular to the axis of flow. The droplet flux density should be described by a bell-shaped curve with a maximum at the centerline of the nozzle \((r = 0)\), or

\[
N = N_{\text{max}} e^{-a_1 r^2}
\]

where \( a_1 \) is a constant which must account for a flattening of the curve as the distance from the nozzle increases. The maximum flux density should be directly proportional to the overall droplet flow rate, and inversely proportional to the square of the axial distance from the nozzle, or

\[
N_{\text{max}} = a_2 \frac{N_0}{z^2}
\]

where \( a_2 \) is a constant of proportionality. To provide a similar widening and flattening of the curve, \( a_1 \) should be equal to \( 1/z^2 \). Combining these conditions leads to
\[ N = a_2 \frac{N_0}{z^2} e^{-r^2/z^2} \quad (3.39) \]

This form satisfies the condition that when \( z \) is much greater than \( r \), the flux density becomes relatively constant. The constant \( a_2 \) may be found by applying the condition that the area integral of the flux density must be equal to the overall flow rate, or

\[ N_0 = 2\pi \int_0^\infty N r dr \quad (3.40) \]

\[ N_0 = 2\pi \int_0^\infty a_2 \frac{N_0}{z^2} e^{-r^2/z^2} r dr \quad (3.41) \]

Solving this equation for \( a_2 \),

\[ N_0 = 2\pi a_2 N_0 \int_0^\infty \frac{r}{z^2} e^{-r^2/z^2} dr \]

\[ 1 = \pi a_2 \int_0^\infty \frac{2r}{z^2} e^{-r^2/z^2} dr \]

Making the substitutions

\[ u = \frac{r^2}{z^2} \]

\[ du = \frac{2rdr}{z^2} \]
\[ 1 = \pi a_2 \int_{0}^{\infty} e^{-u} \, du \]

\[ 1 = \pi a_2 \left[ -e^{-u} \right]_0^\infty = \pi a_2 \]

Therefore, \( a_2 = 1/\pi \), and the expression for the flux density becomes

\[ N = \frac{N_o}{\pi z^2} e^{-r^2/z^2} \quad (3.42) \]

The thickness of the chromium oxide coating will be a function of the droplet flux density, the droplet volume, the solution concentration, the reaction stoichiometry, the time of spraying, and the bulk density of chromium oxide. This dependence can be given in the equation

\[ d_f = \frac{N V d C_s}{\pi z^2} \frac{M_{\text{solute}}}{\rho_{Cr_2O_3}} \frac{t}{M_{\text{Cr}_2O_3}} \quad (3.43) \]

\[ d_f = \frac{N_o V d C_s}{\pi z^2} \frac{M_{\text{solute}}}{\rho_{Cr_2O_3}} \frac{t}{M_{\text{Cr}_2O_3}} e^{-r^2/z^2} \quad (3.44) \]

Using typical values for the experimental apparatus of this project, the constants in this equation may be evaluated to give the thickness as a function of position. Assuming a flow rate of 1.0 cm³/min of a solution of chromium nitrate \([\text{Cr(NO}_3)_5\cdot9\text{H}_2\text{O}]\) in water at a concentration of 0.010 g/ml, and spraying for 10.0 minutes, gives the following equation (see Appendix D for details)
\[ d_f = \frac{1.160 \times 10^{-3} \text{cm}^3}{z^2} e^{-r^2/z^2} \]  

(3.45)

Assuming a distance of 8.0 cm from spray nozzle to substrate gives

\[ d_f = 3.627 \times 10^{-6} \text{ cm} e^{-r^2/64.0 \text{ cm}^2} \]

This function will give film thicknesses of 1813 Å, 1575 Å, and 1369 Å at the center, at the midpoint of an edge, and at a corner of a 6.0 cm square substrate, respectively. An average film thickness of 1659 Å is obtained by integrating this function to a radius such that the area is equal to the area of the square substrate, and dividing by that area.

The efficiency of the spraying system may be calculated by integrating the droplet flux density over that same area, and multiplying by the droplet volume and the time of the spray to find the volume of droplets which may impinge on the substrate.

\[ V = 2\pi V_d t \int_o^{r_m} \frac{N_o}{\pi z^2} \frac{2r}{z^2} e^{-r^2/z^2} \, dr \]  

(3.46)

\[ V = V_d t N_o \int_o^{r_m} \frac{2r}{z^2} \, e^{-r^2/z^2} \, dr \]  

(3.47)

Comparing this volume with the total volume sprayed in this example gives an efficiency of 16.4%.
3.5 Electrostatic Effect

The use of electrostatic precipitation is a possible means to improve the efficiency of the spraying operation. A good summary of this subject is given by Robinson (1973), which is the basis for the following discussion.

An electrostatic precipitation operation includes four major processes. These are corona formation, particle charging, particle migration, and particle collection. The corona formation may be the result of either a negative or a positive discharge. A negative discharge will have free electrons in a high intensity field surrounding the discharge electrode. These electrodes gain energy from the field and produce positive ions and more electrons by collisions with gas molecules. The new electrons are in turn accelerated to produce further ionization in a process referred to as an electron avalanche. The positive ions bombard the negative electrode, giving up high energy and producing secondary electrons. Photoionization, due to high frequency radiation from excited gas molecules within the corona, may also produce secondary electrons. As the electrons move into the weaker field away from the discharge electrode, they form negative ions by attaching to oxygen molecules, thereby forming a dense unipolar cloud of ions between the electrodes. This cloud retards negative emission from the corona and stabilizes the discharge.

Positive corona discharge involves a slightly different mechanism. The electrons formed by ionization in the high intensity field create an electron avalanche which flows in toward the positive electrode.
Positive ions drift into the lower intensity field and do not acquire sufficient energy to produce ionization in the gas or electron ejection from the cathode. Photons originating in the corona cause ionization and generate secondary electrons for a self-sustaining discharge.

In both positive and negative discharge, sparkover will occur as the voltage is increased. However, the negative discharge is more desirable as it has a higher sparkover voltage and will generally yield a higher current at a given voltage.

There are two possible mechanisms for particle charging. Ion bombardment generally predominates for particles greater than a few tenths to one micron, and ion diffusion predominates for particles less than 0.1 micron. In ion bombardment charging, a particle with a uniform surface charge, Q, placed in a uniform field, $E_0$, will distort the field by giving it a radial component, $E_g$. This radial component is defined by a solution to Poisson's equation with appropriate boundary conditions as follows,

$$E_g = -\frac{3V}{3r} = E_0 \cos \theta \left[ 2 \left( \frac{\kappa_p - 1}{\kappa_p + 2} \right) \frac{a^3}{r^3} + 1 \right] + \frac{Q}{4\pi\varepsilon_0 r^2}$$

(3.48)

where $r$ is the radius vector from the center of the particle; $\theta$ is the polar angle between $r$ and the undistorted field, $E_0$; $\kappa_p$ is the relative dielectric constant of the particle; $\varepsilon_0$ is the permittivity of free space, $8.85 \times 10^{-12}$ F/m; and $a$ is the particle radius. An ion of charge $q$ will be attracted to the particle and will impart its charge by
attachment if approaching from an angle for which the radial force, defined by \( F = qEg \), is negative. Letting \( \theta = \pi, r = a, \) and \( p = 2[(\kappa_p - 1)/(\kappa_p + 2)] + 1 \), the maximum free charge on a particle will be

\[
Q_{\text{max}} = 4\pi\varepsilon_0 p a^2 E_o
\]  

(3.49)

The particle charge as a function of time is given by

\[
Q = Q_{\text{max}} \frac{t}{t + \tau}
\]  

(3.50)

where \( \tau \) is a particle charging time constant defined as

\[
\tau = \frac{4\varepsilon_0}{N_0 q b}
\]  

(3.51)

In this equation, \( N_0 \) is the ion density and \( b \) is the ion mobility.

Ion diffusion charging is based on kinetic theory of diffusion. The ion cloud density, \( N \), will vary as

\[
N = N_0 \exp[-U(r)/kT_A]
\]  

(3.52)

where \( U(r) \) is the potential energy of an ion due to its position in the field, \( k \) is Boltzmann's constant, and \( T_A \) is the absolute temperature.

The potential energy of an ion in the vicinity of a charged particle is given by

\[
U = \frac{qQ}{4\pi\varepsilon_0 r}
\]  

(3.53)
where \( q \) and \( Q \) are the charges on the ion and the particle. The time interval, \( t \), associated with collisions is given by

\[
t = \frac{1}{\pi a^2 N \bar{v}_i}
\]  

(3.54)

where \( \bar{v}_i \) is the root mean square velocity of the ions. If all ions impinging on a particle are attached, the charging rate is given by

\[
\frac{dQ}{dt} = \pi a^2 N q \bar{v}_i
\]  

(3.55)

The solution to this equation, for an initially uncharged particle, is

\[
Q = \frac{4 \pi \varepsilon_0 a k T A}{q} \ln \left( \frac{a N q^2 \bar{v}_i}{4 \varepsilon_0 k T A} t + 1 \right)
\]  

(3.56)

The particle migration velocity, \( w \), is dependent on the drag force, \( F \), and the electrostatic precipitating force, \( E_p Q \), where \( E_p \) is the precipitating field. The drag force is given by

\[
F = \frac{1}{2} C_D \pi a^2 \rho g w^2
\]  

(3.57)

where \( C_D \) is a dimensionless drag coefficient dependent on the particle Reynold's number,

\[
Re = \frac{\rho g w (2a)}{\mu}
\]  

(3.58)
where $\rho_g$ and $\mu$ are the gas density and viscosity. In laminar flow ($Re < \nu 1$), $C_D = 24/Re$, and equation 3.57 reduces to Stoke's law,

$$F = 6\pi \mu aw$$

Equating electrostatic and drag forces and solving for the velocity gives

$$w = \frac{2\rho e E' E_a}{3\mu}$$

where $Q$ has been defined as the limiting charge for ion bombardment, and $E'_c$ is the charging field. For single stage precipitation, $E'_c$ is approximately equal to $E_p$. For particles whose size is comparable to the mean free path, $\lambda$, of the gas molecules, $w$ increases by the Cunningham correction factor, $C$, defined by the equation

$$C = 1 + \frac{\lambda}{a} (1.26 + 0.400 e^{-1.10\lambda/a})$$

The Deutsch equation for precipitation efficiency,

$$\eta = 1 - k_A^t$$

was first determined empirically. In this equation, $\eta$ is the fractional efficiency, $t$ is the treatment time, and $k_A$ is a precipitator constant. It was later found that this constant could be evaluated in terms of physically significant quantities. A typical precipitator cross-section has two zones, a laminar boundary layer and a turbulent core. Turbulence
gives a uniform particle concentration, \( C_p \), at a given cross-section. In the boundary layer, a particle has a velocity, \( w \), toward the wall. In the time period \( dt \), particles within a distance \( wdt \) of the wall are precipitated on an area \( dA' \), where \( A' \) is the cumulative collection surface downstream from the precipitator inlet. The particle concentration opposite \( dA' \) will be reduced by \( dC_p \). Equating loss from the gas and accumulation on the surface gives

\[
V \frac{dC_p}{dA'} = -wC_p \frac{dA'}{dA'}
\]

Integrating this equation and defining efficiency in terms of inlet and outlet concentrations gives

\[
\eta = 1 - \frac{C_{out}}{C_{in}} = 1 - e^{-A'w/V_g}
\]

where \( V_g \) is the gas volumetric flow rate.

Using these equations it is possible to calculate an efficiency for electrostatic spraying with the apparatus of this project. An electrostatic field strength of \( 3.00 \times 10^5 \) V/m will give the particles a migration velocity of 4.24 cm/sec (see Appendix E for details of these calculations). With a substrate area of 36.0 cm\(^2\) and an air flow rate of 605 cm\(^3\)/sec, the calculated efficiency is 22.3 percent. Field strengths of \( 6.00 \times 10^5 \) V/m and \( 8.00 \times 10^5 \) V/m will give efficiencies of 63.5 percent and 83.4 percent, respectively.

When the spray distribution is taken into consideration, the overall efficiency will be lower than the electrostatic collection
efficiency. If the discharge electrode is a screen 15.0 cm square, mounted perpendicular to the spray direction, and a distance of 8.0 cm from the nozzle, only 67.3 percent of the droplets will pass through the screen to become charged. The resulting overall efficiencies corresponding to the above field strengths then become 15.0 percent, 42.7 percent, and 56.1 percent. These efficiencies indicate a considerable improvement over spraying without electrostatics.
CHAPTER 4

EXPERIMENTAL PROGRAM

As the primary purpose of this project was to study low-cost film deposition techniques, considering the possibility of scaling up to commercial size if the process proved feasible, an attempt was made to keep the experimental program as simple as possible. Details of the apparatus and procedures used are discussed in the following sections.

4.1 Experimental Apparatus

The major items of equipment used in this project included a holding vessel to supply the chromium solutions, a flowmeter for solution flow rates, a spray nozzle with high-pressure air supply, and a hot plate. For the electrostatic experiments, a high-voltage DC power supply was also used. A schematic diagram of this apparatus is given in Figure 4.1.

The spray nozzle was the single most important part of the apparatus. The Sonicore 035H nozzle, made by the Sonic Development Corporation, was selected for its atomization characteristics. This nozzle makes use of a resonator chamber which creates a standing shock wave of high-frequency sound vibrations to thoroughly atomize the liquid. The main features of the nozzle are illustrated in Figure 4.2. The nozzle itself and the core are constructed of 406 stainless steel, while the adapter is a brass alloy. With an air flow rate of 1.1 scfm
Figure 4.1 Diagram of Experimental Apparatus. -- 1. Burette for chromium solutions. 2. Rotameter. 3. Sonicore 035H nozzle. 4. Wire screen discharge electrode. 5. Hot plate. 6. Pressure gage. 7. Pressure regulator. 8. Air filter. 9. High voltage DC power supply.
Figure 4.2 Diagram of Sonicore 035H Nozzle. -- Approximately twice actual size.
at 44 psig, up to 10.0 cm$^3$/min of solution may be atomized to a maximum droplet size of one micron. The air supply for the nozzle was through the high-pressure air system of the Department of Chemical Engineering. The air was filtered to remove oil, water, and scale, and was regulated to the desired pressure for operation.

For the first several experiments, a stainless steel holding tank was used for the chromium solutions. However, in order to obtain a more accurate value for the volume of solution sprayed, the tank was replaced with a standard 25 ml glass burette with a three-way, Teflon stopcock.

The solution flow rate was measured by means of an RGI rotameter, number G835. Because no calibration curve was available, data were taken for the flow rate as a function of the reading. These data are included in Appendix A and are plotted in Figure 4.3. For the first several tests, the volume sprayed was estimated from the average flow rate and the time of spraying. After installation of the burette, the flowmeter was primarily used to maintain a constant flow rate of solution during the tests.

The substrates were heated to the desired temperatures with a Thermodyne Type 1900, Model HP-A1915B, hot plate, made by the Sybron Corporation. The surface temperature of the hot plate, as a function of the control position, was calibrated using a thermocouple with direct digital temperature readout. The data are included in Appendix A, and a plot of the data is shown in Figure 4.4.
Figure 4.3 Calibration Curve for RGI -- G835 Rotameter.
Figure 4.4 Calibration Curve for Thermodyne, Type 1900 Hot Plate.
The tests were timed with a Time-It Electronic Stopwatch from Precision Scientific Co., with a counter reading to hundredths of a minute. A Mettler H10T Balance, from the Mettler Instrument Corp., with digital readout to 0.1 mg, was used to determine the substrate masses before and after the spraying, and also in preparation of the solutions.

For the tests using electrostatic deposition, a Regulated High Voltage DC Power Supply, Model RG-10, from the Spellman High Voltage Company, was used. This power supply has a variable output from eight to twelve kilovolts, with a maximum current of two ma. For some tests, the high-voltage lead was attached directly to the spray nozzle, but for later tests it went to a wire screen between the nozzle and the grounded substrate. A vertical orientation, with the screen and plate both parallel to the direction of the spray, was also tried.

Samples that appeared satisfactory in a visual inspection were scanned for reflectance as a function of wavelength to determine selective surface qualities. For wavelengths in the long visible to near-infrared region (0.6 μm to 2.7 μm), a Perkin-Elmer 450, Ultraviolet-Visible-Near Infrared Spectrophotometer was used. For the longer infrared region (2.5 μm to 15 μm), a Perkin-Elmer 137, Sodium Chloride Spectrophotometer was used. Both of these instruments were available in the Department of Optical Sciences of The University of Arizona.

The substrates used for the first few trials were polished, heavy aluminum sheet, available as scrap in the shop. For most of the experiments, Coilzak was used as the substrate. It is a lightweight aluminum sheet from Alcoa, with one highly polished side protected by an
adherent paper coating. This coating was not removed until everything else was ready for testing. After discovering problems with the Coilzak substrates, another type of aluminum was needed. The alloy used for the final tests was Kaiser-AN-080, 6061-T6-QQ-A-250/11. Individual substrates of this material were cut with a band saw and polished with a buffing wheel.

Tests were made using different compounds of chromium. Solutions of chromium nitrate \([\text{Cr(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}]\) were prepared with distilled water at concentrations from 5.0 to 15.0 g/l. Crystals from J. T. Baker Chemical Co., with a minimum purity of 98.6 percent, were used. A solution of 10.0 g/l of chromium acetylacetonate \([\text{Cr(C}_5\text{H}_7\text{O}_2\text{)}_3]\) powder from the Shepherd Chemical Co. was prepared and tried using acetone as the solvent. Chromium trioxide crystals, from Mallinkrodt Chemical Works, with a purity of 98.0 percent, were used in a distilled water solution at 5.0 g/l.

4.2 Experimental Procedure

The procedure described below was developed over the course of the experimental work as minor modifications were made to improve the efficiency of the testing and the accuracy of the measurements. Prior to the actual spraying, it was necessary to prepare the chromium solutions. The mass of the compound used was determined on the Mettler balance, and the solutions were mixed in a volumetric flask of the desired volume, usually 100.0 ml.

For different solutions, it was necessary to completely disassemble and clean the spray apparatus. The nozzle core could be
removed to be certain that the air passage and the liquid orifices were not obstructed. After reassembly, the solution was added to the system through the burette. Care was taken to eliminate air from the system between the burette and the nozzle.

If not already in use, the air compressor had to be turned on and allowed to develop sufficient pressure. The pressure delivered to the nozzle was measured with gages and set to the desired pressure with a regulator.

After a substrate had been cut out and polished, its mass was determined on the Mettler balance. The substrate was heated on the hot plate, and when it reached the desired temperature it was ready to be sprayed.

The spraying was started with the burette filled past the zero point and a cover over the substrate. The valve on the air line was opened fully, and the valve controlling the solution flow was opened to give the desired flow rate through the rotameter. When the solution level reached the zero point in the burette, the substrate was uncovered and the time was started. During the spraying, the solution control valve was adjusted as necessary to maintain the proper flow rate. After the desired period of time, the substrate was covered again, and the solution and air valves were closed. The volume of solution sprayed could be read directly from the burette.

After spraying, the hot plate was adjusted to the desired baking temperature to complete the conversion to chromium oxide (Cr₂O₃). Following this baking period, the substrate was cooled, and its final mass
was determined with the Mettler balance. The difference between final and initial masses was due to the chromium oxide deposited. An efficiency for the spray could be calculated by comparing the amount deposited with the stoichiometric amount available in the solution. An average film thickness could be calculated using the substrate dimensions and the bulk density of chromium oxide.

The procedure followed for electrostatic spraying was virtually identical with that described above, with the exception that the high-voltage supply was turned on and adjusted to the desired voltage after uncovering the substrate. At the end of the spraying time period, the power supply was turned off before covering the substrate.

Due to the nature of these experiments, certain safety precautions were necessary. As the chromium solutions may cause minor skin irritation, excessive contact with the solutions was avoided. All experiments were conducted in a fume hood to control toxic vapors. Decomposition of the chromium nitrate gave off nitric oxide, and acetone vapors and organic decomposition products were released when using chromium acetylacetonate. When using electrostatic deposition, care was taken to avoid any contact with the high-voltage electrode. This electrode was carefully insulated from the rest of the experimental apparatus. After turning off the power supply, a grounded probe with an insulated handle was used to be certain that there was no residual charge on the equipment.
4.3 Experimental Variables

During the course of the experimentation, a number of conditions were varied in an attempt to produce satisfactory coatings. The temperature of the hot plate was varied between 150°C and 450°C during spraying. Baking times ranged from 20 minutes to one hour, at temperatures from 150°C to 450°C. The height of the spray nozzle could be changed by altering the pipe fittings in the supports. Distances between 6 and 30 centimeters were used. The atomizing air pressure was adjusted between 36 and 48 psig by means of the regulator. Solution concentrations of 5.0 g/l, 10.0 g/l, and 15.0 g/l were tested, and flow rates were varied from 0.8 ml/min to 4.75 ml/min. In the experiments with electrostatics, voltages from 8.0 kV to 12.0 kV were used, with field strengths varying from 3.0 to 10.0 statvolts/cm.
The thin films produced during the experimental portion of this project were not totally satisfactory. Much time was spent in an effort to find materials and conditions which would lead to reasonably consistent results. In this respect, this project may serve as the basis for further research into the solution spraying technique for chromium oxide coatings on aluminum.

5.1 Physical Characteristics of Films

From a physical standpoint, the overall quality of the thin films may be discussed in terms of adhesion, uniformity of thickness, and surface roughness. The adhesion of the surfaces turned out to be strongly dependent on experimental conditions. The non-uniformity of coating thickness is probably the major drawback to the apparatus used in this experiment. A certain amount of surface roughness is inherent in any spraying operation, but hopefully it will not significantly affect the optical characteristics of the selective surface.

Typical coatings shown in Figures 5.1 through 5.6 illustrate several interesting features of the coatings produced with this apparatus. These photographs were taken with an American Optical microscope with a Polaroid camera attachment at a magnification of one hundred times. Figure 5.1 (Substrate No. 48) shows the surface of the
Figure 5.1 Substrate No. 48, Polished Aluminum Surface.

Figure 5.2 Substrate No. 66, Rough, Flaky Coating.
Figure 5.3 Substrate No. 73, Thin Coating before Baking.

Figure 5.4 Substrate No. 70, Thin Coating after Baking.
Figure 5.5  Substrate No. 72, Thick Coating before Baking.

Figure 5.6  Substrate No. 71, Thick Coating after Baking.
aluminum alloy, 6061-T6, after polishing with the buffing wheel. This surface is generally very smooth, with some indication of scratches which were not removed during polishing.

The rough surface pictured in Figure 5.2 (Substrate No. 66) was prepared by spraying at 250°C and baking at 450°C. During the baking, the thin film of chromium oxide cracked and peeled, forming flakes in the size range of ten to twenty microns. Surfaces of this type have very poor adhesion, being easily rubbed off with a finger, and are obviously unsuitable as solar energy collectors.

Figures 5.3 and 5.4 (Substrates No. 73 and No. 70) illustrate very thin films (~500 Å), with incomplete coverage, before and after baking, respectively. Figure 5.3 clearly shows that the deposition occurs as discrete units distributed over the surface. The average size of the spots of chromium nitrate is about twenty microns, which suggests that the spray droplet size may be considerably larger than the one micron claimed by the nozzle manufacturer. It is possible that excessive coalescence of smaller droplets occurred. Figure 5.4 shows a similar surface, with a slightly higher spot density, after baking for one hour at 450°C. During baking, the chromium nitrate is converted to chromium oxide, and the spots appear considerably flatter and indicate a tendency to spread out to give a better coverage of the substrate.

Figures 5.5 and 5.6 (Substrates No. 72 and No. 71) show thicker films (~2000 Å) which completely cover the substrates. The unbaked chromium nitrate surface of Figure 5.5 appears fairly rough, with a grain size on the order of ten microns. The surface of the substrate in
Figure 5.6 has been baked for two hours at 450°C to complete the conversion from chromium nitrate to chromium oxide. The baking has apparently smoothed the surface, with the irregularities being on the order of a few microns.

The substrate temperature during spraying is probably the most significant factor affecting coating adhesion. Early experimental results suggested that a moderate hot plate temperature, around 170°C to 180°C, would be most desirable. Temperatures below this range allowed the spray to cool the substrate surface to the point of allowing liquid droplets to collect on the surface. The presence of liquid on the surface always resulted in a very heavy, localized deposit, with poor adhesion, as the solution evaporated. Hotter temperatures, from 200°C to 250°C, seemed to give more even coatings, but with poor adhesion. However, the results of these early tests were not always consistent, and the good adhesion noted on some substrates was probably due to factors other than temperature alone.

Three series of tests (Substrates Nos. 58-61, Nos. 62-65, and Nos. 66-69) were conducted holding all factors constant except temperature, which was varied from 250°C to 400°C. In each of these series, the substrate at 250°C produced a coating with very poor adhesion. Microscopic examination revealed that the surfaces were cracked and flaking, probably due to thermal stresses created during baking by the different coefficients of thermal expansion for the film and the substrate. The substrates at 300°C and 350°C gave better surfaces with generally good adhesion. At 400°C there was very little coating
deposition, possibly because the spray droplets were totally evaporated before impinging on the substrate, allowing the extremely small solid particles to be carried away in the air stream.

A baking period after spraying was necessary to convert the chromium nitrate, or other spray chemical, to the desired chromium oxide film. In the case of chromium nitrate, the baking caused a fairly rapid color change on the surface from light green to dark brown to black, accompanied by noticeable evolution of nitrous oxide. This physical appearance suggested that the baking could be completed in twenty to thirty minutes at a temperature of 350°C. Several substrates were baked at 250°C to test whether this could provide improved adhesion, but there was no significant difference. Later, infrared scans revealed that an extended baking period of one to two hours, depending on the film thickness, at 450°C may be necessary to complete the conversion to the desired chromium oxide. These tests will be described in more detail in Section 5.2.

The Sonicore 035H nozzle selected for these experiments proved to be unsatisfactory for this application. While it is an excellent atomizing nozzle, it has certain drawbacks which interfere with its use for spray coatings. It requires a fairly high air pressure and volume to obtain atomization, and this in turn affects the possibility of atomized droplets impinging on and becoming attached to the substrate due to the excessive air flow. The small openings for liquid and air passage through the nozzle could become plugged fairly easily, requiring complete disassembly for cleaning. If the nozzle core was not
sufficiently tightened into the atomizer during assembly, the nozzle would pulse badly, giving uneven liquid flow and very poor atomization. Operating the nozzle at a liquid flow rate below the minimum recommended by the manufacturer may have also contributed to the pulsing effect. This condition often led to the collection of excess liquid on the substrate, resulting in an unsatisfactory coating. Unfortunately, the nozzle core is machined such that its walls are very thin, and one core was destroyed by merely tightening it into the atomizer with a small wrench.

The height of the spray nozzle above the substrate was varied to determine whether it would have any effect on the coating quality. Nozzle heights between eight and twelve centimeters generally produced the best results. At closer nozzle distances, the high air velocity interfered with deposition on the surface, and at greater distances, the spray was spread out to the point that very little deposition occurred.

An air pressure of 44 psig was recommended by the nozzle manufacturer for the minimum liquid flow rates. Attempts to use lower pressures resulted in insufficient atomization, and greater pressures adversely affected deposition due to increased air velocity and turbulence.

Solution concentrations of ten grams of solute per liter of spray solution were used in most of the tests. Solutions of five and fifteen grams per liter were also tested, but they showed no obvious advantages or disadvantages. It is speculated that higher concentrations may reduce film adhesion because of faster deposition, and lower
concentrations require much higher liquid flow rates to maintain a reasonable film deposition rate. However, these possibilities could not be adequately examined due to the inconsistent nozzle performance which had a severe effect on film quality.

Solution flow rates of around one to one and a half milliliters per minute appeared to give the best results with this nozzle. Extremely low flow rates caused poor nozzle performance due to excessive pulsing. Higher flow rates, closer to the manufacturer's recommended range, allowed more efficient atomization, but turbulence prevented the extremely fine particles from becoming attached to the substrate. Again, nozzle inconsistency prevented an effective study of this problem.

Of the three chromium compounds used, only chromium nitrate \([\text{Cr(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}]\) produced acceptable films. Chromium acetylacetonate \([\text{Cr(C}_5\text{H}_7\text{O}_2\text{)}_3]\) was tried on Substrate No. 18, being sprayed in an acetone solution. Nozzle performance was adversely affected by a buildup of the chromium acetylacetonate on the atomizing tip due to the rapid evaporation of the acetone upon leaving the spray nozzle. A coating was visible on the substrate after spraying for ten minutes with a hot plate temperature of 100°C. However, when the temperature was raised to 200°C to convert the coating to chromium oxide, it sublimed and totally disappeared, leaving a clean surface within ten minutes. When other researchers have obtained oxide films from chromium acetylacetonate, they used more extreme spray conditions not possible with this apparatus.

Chromium trioxide \((\text{CrO}_3\text{)}\) in a water solution was used for Substrate No. 22. Spraying with a hot plate temperature of 180°C gave a
thin, yellowish film, but this film did not turn black as expected after baking for one hour at 400°C. It is possible that the film was too thin to show any visible change, and further tests should probably be tried with chromium trioxide, especially in light of the infrared results for the chromium nitrate tests.

The decomposition of chromium nitrate appears to proceed in the following two steps:

1. \[ \text{Cr(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \rightarrow \text{CrO}_3 + 3\text{NO}_2^+ + 9\text{H}_2\text{O}^+ \]

2. \[ 2\text{CrO}_3 \rightarrow \text{Cr}_2\text{O}_3 + 1 \frac{1}{2} \text{O}_2^+ \]

An infrared reflectance scan of Substrates No. 71 and No. 75 before baking showed very strong chromium nitrate peaks. After baking for one hour at 450°C, the nitrate peaks had disappeared and in No. 75 were replaced by strong CrO₃ peaks. Substrate No. 71 had a much thinner coating and showed only weak CrO₃ peaks. After another hour at 450°C, the CrO₃ peaks disappeared and the conversion to Cr₂O₃ was completed. These scans will be discussed further in Section 5.2.

The aluminum sheet used for the first eight tests had a very poor quality surface and was not expected to produce good films. It was used primarily to develop a spraying technique and to work out any problems with the spraying system. These substrates were too large, at ten centimeters square, to be covered satisfactorily, and they were not highly polished.

The Coilzak aluminum used for Substrates No. 9 through No. 47 was cut to six centimeter squares to try to obtain better coverage. The highly polished surface of this material was highly reflective to
visible light. Unfortunately, infrared scans of coatings on this material revealed a clear, anodized surface of hydrated aluminum oxide. This material is strongly absorbing in the medium-to-long infrared wavelengths. This heavy, anodized layer explains that the masses of some of these substrates were less after spraying and baking due to the loss of water by hydration in the aluminum oxide.

The aluminum sheets, 6061-T6, used as the substrate for the final tests appears to be very satisfactory for use in a solar energy collector. The infrared reflectance curve for a polished sample of this material was very close to that for an evaporated aluminum standard. Satisfactory coatings were deposited on this aluminum, and it is strong enough to be used as a construction material for a solar panel.

The tests attempting to use electrostatic deposition were totally unsuccessful. In the first three trials (Substrates No. 33, No. 34, and No. 35), the high-voltage source was connected directly to the nozzle. This arrangement was unsatisfactory for a number of reasons. When the nozzle was too far from the substrate, the electrostatic field strength was too low to have any effect on the deposition. Moving the nozzle closer increased the field strength, but it was overpowered by the turbulence created by the high nozzle velocity. This system also has an uneven field strength acting on the spray, due to varying distances between the nozzle and different areas of the substrate.

In the next series of tests, the high-voltage supply was connected to a wire screen discharge electrode located between the nozzle and the substrate, and oriented parallel to the substrate. In this
arrangement, a constant field strength was acting on the spray. A serious drawback with this system was that, in each test, the spray collected on the screen, and large drops then fell to the substrate. On Substrate No. 36, a grid pattern was visible after spraying and baking, apparently due to a shadow effect from the screen. This uneven distribution suggests that the electrostatics had very little influence on the spray pattern. During the spraying of Substrate No. 37, some arcing occurred between the discharge electrode and the substrate, indicating that the field strength of 10.0 statvolts per centimeter should not be increased.

A third orientation for electrostatic deposition was also tested. A wire screen was again used as the discharge electrode, and both the screen and the substrate were vertical and parallel to the axis of the spray nozzle. This system was also ineffective for coating as neither Substrate No. 44 nor Substrate No. 43, sprayed with and without electrostatic voltage, respectively, showed any deposition. This orientation was also used for two substrates which were cooled to 0°C prior to spraying in an attempt to improve deposition by condensation on the substrates. These substrates, No. 46 and No. 45, were sprayed with and without electrostatics, and as expected there was no deposition on either substrate.

5.2 Optical Properties of Films

The infrared reflectance scans run on a number of the substrates proved to be very useful for determining the chemical composition of the substrate surface as well as for examining the selective surface
characteristics. The first scan, on Substrate No. 41, gave very surprising results between 2.5 and 15 microns. The Coilzak substrate coated with chromium oxide was expected to be highly reflective in this range, but instead it showed strong absorptance, with major peaks at 3 μm, 8.7 μm, and 10.7 μm, and lesser peaks at 3.6 μm, 4.8 μm, and 5.3 μm (see Figure A.1). A scan of the uncoated side of this substrate and a scan of an untreated polished surface of Substrate No. 47 showed similar features. Subsequent comparison with literature data (Frederickson 1954; Sadtler Standard Spectra 1965, spectrum Y175K) revealed that the Coilzak has a heavy surface coating of hydrated aluminum oxide. These results made it necessary to find another material for substrates.

An infrared scan of a polished aluminum substrate, No. 48, was run prior to using this material in the spray tests. The reflectance of this material was close to that of an evaporated aluminum standard throughout the range of interest.

Substrate No. 51 also showed some interesting features in the infrared region. This sample was covered with a fairly heavy, even black coating and a strong absorptance peak at 3.1 μm and a broad peak at 11.7 μm (see Figure A.2). This spectrum compares quite well with literature data for CrO₃ (Sadtler 1965, spectrum Y53K). Substrate No. 53 had a much thinner film which showed absorptance at 3.1 μm, but very good reflectance beyond 7 μm (see Figure A.2), indicating that the black surface was transparent in the infrared region. This film was most likely Cr₂O₃ (Sadtler 1965, spectrum Y297K), with some CrO₃ to cause the feature at 3.1 μm.
Infrared scans from 2.5 μm to 15 μm were run on Substrates No. 55 and No. 56 (see Figure A.3); No. 59, No. 60, and No. 61 (see Figure A.4); and No. 63 and No. 68 (see Figure A.5). These coatings all appear to be mixtures of \( \text{CrO}_3 \) and \( \text{Cr}_2\text{O}_3 \) in varying proportions. Substrates No. 55, No. 56, and No. 60 show the strongest \( \text{CrO}_3 \) features, while Substrates No. 61 and No. 63 contain very little \( \text{CrO}_3 \). The scans consistently show that the thicker films have lower infrared reflectance and are less completely converted to \( \text{Cr}_2\text{O}_3 \).

Following up on these results, three more substrates, No. 70, No. 71, and No. 75, with estimated film thicknesses of 600 Å, 2000 Å, and 5000 Å, respectively, were scanned from 2.5 μm to 15 μm. The first scan was run after these substrates were sprayed at a hot plate temperature of 350°C, but before they were baked (see Figure A.6). Substrate No. 70 showed a slight indication of \( \text{CrO}_3 \) at 3.1 μm, but it had generally good reflectance over this range. Substrates No. 71 and No. 75 showed very strong absorptance peaks around 3 μm and between 6 μm and 8 μm. Substrate No. 75 consistently gave a lower reflectance than No. 71. These features match very well with literature data for \( \text{Cr(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) (Sadtler 1965, spectrum Y205K). After baking for one hour at 450°C (see Figure A.7), Substrate No. 70 showed no evidence of \( \text{CrO}_3 \), and beyond 7 μm its reflectance was very close to that of the evaporated aluminum standard. Substrate No. 71 showed the \( \text{CrO}_3 \) feature at 3.1 μm, but its reflectance increased to match that of No. 70 beyond 7 μm. Substrate No. 75 showed very strong absorptance due to \( \text{CrO}_3 \) beyond 9.5 μm, indicating a large proportion of \( \text{CrO}_3 \) in the coating. After baking
Substrates No. 71 and No. 75 for an additional hour at 450°C, the absorptance peaks due to CrO$_3$ disappeared, indicating that the conversion to Cr$_2$O$_3$ was completed (see Figure A.8). Substrate No. 75 showed consistently lower reflectance than Substrate No. 71.

These results confirm that the conversion of chromium nitrate to chromium oxide proceeds in two steps with chromium trioxide as an intermediate product. The longer times required for the conversion of thicker films support this mechanism, with the reaction rates controlled by diffusion of the gaseous products through the solid film.

Attempts to scan the reflectance of several substrates in the middle visible to the near-infrared region (0.6 μm to 2.7 μm) provided less satisfactory results. The scans showed generally low reflectances which tended to increase slightly with increasing wavelength. However, the data are misleading because the instrument used measured only normal reflectance. This range of wavelengths is of the same order as the grain size observed in microscopic examination of the coatings, thereby leading to an undetermined amount of scattered radiation which was not absorbed or detected by the reflectance scan. To properly evaluate the reflectance in this region, an instrument capable of measuring total hemispherical reflectance is necessary. There is an instrument of this type in the Department of Optical Sciences, but it was not available during the time these scans were run.

5.3 Comparison with Theory

A strict, quantitative comparison of the experimental results with the spray distribution and film thickness model developed in
Section 3.4 is not possible, primarily due to the extreme inconsistencies in the performance of the spray nozzle. Severe pulsing in the nozzle generally caused the collection of liquid on the substrate, followed by redistribution due to the high gas flow rate. The calculated film thicknesses and spray efficiencies tabulated in Tables A.1 and A.2 (Appendix A) may be somewhat misleading. These values are based on the overall mass difference of a substrate before and after spraying and baking, and the calculations assume complete conversion of chromium nitrate to chromium oxide. The infrared results discussed in Section 5.2 revealed that the conversion is generally not complete and is itself a function of the film thickness. The presence of $\text{CrO}_3$ in the film will lead to errors in the calculated film thickness because its density is only 2.80 g/cm$^3$ compared with 5.21 g/cm$^3$ for $\text{Cr}_2\text{O}_3$. A film containing ten percent $\text{CrO}_3$ would have a calculated film thickness 8.5 percent less than the actual thickness. Fifty percent $\text{CrO}_3$ would give a calculated film thickness 31.7 percent less than the actual. Errors in mass determination also lead to errors in the calculated film thicknesses. An error of 0.2 mg in a film mass of 1.0 mg would give a film thickness error of 20 percent. The same error of 0.2 mg in a film mass of 3.0 mg would lead to an error of only 6.7 percent in film thickness. Another potential source of error would be from oxidation of the aluminum substrates during baking. However, it is felt that this is not a serious problem because the front surfaces of the substrates were protected by a chromium oxide coating, and the back surfaces were already covered with an aluminum oxide layer. Another difficulty with these calculations for the Coilzak substrates is the variation in the water of hydration in the
anodized surface. In several cases, the final mass of a substrate was less than the initial mass.

From a more qualitative point of view, however, the model does seem to fit the observed results reasonably well. The calculated average film thickness and spraying efficiency from Section 3.4 for typical experimental conditions fit well within the range of values given in Table A.1.

On almost all of the substrates, the film thickness showed wide variations, with some portions of the substrate heavily covered and other portions practically clean. In many cases this showed up as a very distinct radial pattern. Substrate No. 27 is one of the better examples of this effect. After spraying and baking, the coating on this substrate showed four distinct zones in a concentric pattern. The center zone, with a diameter of 1.4 cm, was the heaviest, with a black coating covered with small bumps. This zone had only fair adhesion. The next zone, with a width of about 0.7 cm, had a smooth black coating with good adhesion. This type of coating would be the most desirable for a solar energy collector. The third zone, also with a width of about 0.7 cm, had a gray spotty coating with poor adhesion. The fourth zone, covering the remainder of the substrate, had a thin, yellowish coating which became visibly thinner with increasing radius. The thickness difference from the center to the edge of this substrate appears to be much greater than that predicted by the distribution model. This difference suggests that the actual spray distribution may be much more concentrated than the bell-shaped curve used in the model. Another explanation is also possible, however. The coating on the substrate should result from
spray droplets coming in direct contact with the surface. Droplets farther from the axis of the spray nozzle would have less vertical velocity and would be more affected by the radial flow of the air stream as it approached the surface, thereby resulting in a reduced tendency for impingement with increasing radius.

As discussed in Section 5.2, the infrared reflectance spectra of the experimental thin films can be compared quite closely to the literature data available, allowing a qualitative determination of the chemical composition of the film. The reflectance data collected suggest that the films do have selective surface characteristics. For example, Substrate No. 53, with an estimated film thickness of 975 Å, showed high reflectance beyond a wavelength of 7 μm and strong absorptance below 1 μm. However, the data at the lower end of this range are questionable due to the scattering effect discussed previously. The overall effect is similar to that of a good selective surface as illustrated in Figure 3.2, except that the experimental absorptance and reflectance are not as extreme as the ideal case, and the transition from absorptance to reflectance is much more gradual between 2 μm and 7 μm.

A quantitative comparison of the experimental reflectance with the theoretical reflectance calculated with the equations in Section 3.2 is not possible for several reasons. As can be seen from Figure 3.4, the reflectance of a selective surface is very sensitive to the film thickness, and there was no accurate means available to measure the thickness of the experimental films. Another problem is that very little data are available for the optical constants of chromium oxide, and the data that were found fell within the range in which the experimental reflectance is most affected by scattering.
CHAPTER 6

CONCLUSIONS

The solution spraying techniques for chromium oxide selective surfaces as developed in this project were only partially successful. It has been demonstrated that thin films of chromium oxide on aluminum may be prepared by the thermal decomposition of chromium nitrate sprayed in a water solution. These coatings were shown to have optical characteristics suitable for selective solar energy absorption. However, inconsistent performance of the spray nozzle made it impossible to reproduce results at constant conditions. The normal atomization characteristics of the nozzle also prevented the preparation of films with a constant thickness across the substrate. The actual films showed a very noticeable radial thickness variation, similar to that predicted by the spray distribution model for this nozzle. A number of spray condition variables which were examined, such as nozzle height, air pressure, and, to a lesser extent, solution flow rate, are specific to this nozzle and would not be applicable with other nozzles.

One of the most important variables affecting the final film quality is the hot plate temperature. A temperature of 350°C appeared to produce the best films. This variable should be independent of the nozzle used, but it is probably specific for spray solutions of chromium nitrate in water. At lower hot plate temperatures, the films had poor
adhesion due to cracking and flaking caused by thermal stresses created during baking. At higher temperatures there was very little deposition during spraying, probably due to complete evaporation of the solution before droplets could impinge on the substrate.

Of the three chromium solutions used, only the chromium nitrate in water produced satisfactory films. The solutions generally contained ten grams of solute per liter of solution, but concentrations of five and fifteen grams per liter were also tried and showed no obvious advantages or disadvantages. The hot plate temperature of 350°C during spraying and the baking temperature of 450°C for the chromium nitrate solutions turned out to be much more severe than anticipated at the beginning of this project, but these temperatures are still below those required for normal vapor deposition techniques. A solution of chromium acetylacetonate in acetone proved to be unsatisfactory for low temperature application. A coating visible on the substrate after spraying at 100°C was totally removed by sublimation when the temperature was raised to 200°C for baking. Chromium trioxide in a water solution gave a thin, yellowish film which did not turn black as expected during baking. However, because chromium trioxide has been shown to be an intermediate product in the decomposition of chromium nitrate, further tests would be in order.

The aluminum sheet, 6061-T6, is highly reflective in the infrared region and should be suitable as a construction material for full-scale solar panels. The Coilzak substrates, used in early tests, although highly reflective in the visible wavelengths, are unsatisfactory for a
solar energy collector due to the heavy coating of hydrated aluminum oxide.

The electrostatic apparatus used in this project was totally unsatisfactory. This failure was at least partially due to the high air pressure and volume required for atomization in the nozzle which overpowered the electrostatic forces acting on the spray droplets. Electrostatics still have the potential for producing films of constant thickness if applied with more appropriate apparatus.

Infrared reflectance scans proved to be very useful for determining the chemical composition of the films after spraying and baking. A series of scans on several substrates showed clearly that the decomposition of chromium nitrate to chromium oxide proceeds in two steps with chromium trioxide as an intermediate product. Infrared scans also revealed the hydrated aluminum oxide coating on the Coilzak and showed that the polished aluminum, 6061-T6, reflectance is almost as good as that of an evaporated aluminum standard.

Shorter wavelength scans, from the visible to the near-infrared range, were less satisfactory. They showed very little normal reflectance, but this is due to scattering as well as absorptance. It was not possible to distinguish between these two effects with the equipment available during the testing period. However, the overall optical effect appears to show promise as a selective surface with strong absorptance in the visible range, strong reflectance in the infrared, and a transition zone at wavelengths between two and seven microns.
In summary, thin films of chromium oxide were obtained by spraying water solutions of chromium nitrate onto a polished aluminum substrate at moderate temperatures. After baking, these films showed selective surface characteristics of absorptance in the visible range and reflectance in the infrared range. The results suggest that some modification of the technique used in this research may be suitable for making full-scale solar energy collector panels.
RECOMMENDATIONS FOR FURTHER STUDY

The limited success of this project indicates that further research in solution spraying techniques would be desirable. One point of primary concern would be the selection of a more effective and consistent spray nozzle. It would be better to use a nozzle which could provide sufficient atomization at low solution flow rates with a minimum gas pressure and flow rate. For improved efficiency and better control over film thickness, the spray distribution from the nozzle should be relatively constant at a reasonable distance from the nozzle. The possibility of a spray nozzle specifically designed for electrostatic deposition should also be considered.

If high quality, constant thickness films are obtained on small substrates, additional testing is possible. Static tests of solar energy absorption could be conducted by placing the substrates in direct sunlight and measuring the temperatures obtained. For better control of the spraying operation, it would be desirable to have a radiation pyrometer to measure the actual substrate temperature during spraying. Relying on the hot plate temperature is not totally satisfactory. Additional infrared and visible reflectance data on the films are necessary. Due to the grain size in the films, an instrument to measure total hemispherical reflectance is needed to separate the effects of absorption
and scattering in the visible and near-infrared regions. Interpretation of results would be improved by an exact measurement of the film thickness, which should be possible with the use of X-ray diffraction.

If testing on the small substrates is satisfactory, the next step should be to construct medium scale aluminum panels with channels for a heat transfer fluid, probably water. It would be necessary to develop a spraying apparatus to give a film of constant thickness across the whole panel. This might be possible through the use of several nozzles in a line and moving the panels past the nozzles at a constant rate. Panels produced by this method could then be flow tested and compared with other selective surface panels currently available. A final consideration would have to be an economic evaluation of this procedure to determine whether any cost differences between these panels and others would be offset by improved performance.
<table>
<thead>
<tr>
<th>Substrate Number</th>
<th>Soln. Conc. (g/l)</th>
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<td>2038</td>
<td>34.5</td>
</tr>
<tr>
<td>38</td>
<td>1.25</td>
<td>7.65</td>
<td>11.8</td>
<td>12.0</td>
<td>10.0</td>
<td>180</td>
<td>250</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>39</td>
<td>1.25</td>
<td>6.00</td>
<td>11.8</td>
<td>12.0</td>
<td>10.0</td>
<td>180</td>
<td>450</td>
<td>552</td>
<td>8.8</td>
</tr>
<tr>
<td>43</td>
<td>1.25</td>
<td>11.55</td>
<td>24.3</td>
<td>0.0</td>
<td>0.0</td>
<td>--</td>
<td>150, 450</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>44</td>
<td>1.25</td>
<td>12.30</td>
<td>24.3</td>
<td>12.0</td>
<td>10.0</td>
<td>--</td>
<td>150, 450</td>
<td>55</td>
<td>0.4</td>
</tr>
<tr>
<td>45</td>
<td>1.25</td>
<td>1.20</td>
<td>24.3</td>
<td>0.0</td>
<td>0.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>46</td>
<td>1.25</td>
<td>0.70</td>
<td>24.3</td>
<td>12.0</td>
<td>10.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
Figure A.1 Infrared Reflectance, Substrate No. 41.
Figure A.2 Infrared Reflectance, Substrates Nos. 48, 51, and 53.
Figure A.3 Infrared Reflectance, Substrates Nos. 55 and 56.
Figure A.4  Infrared Reflectance, Substrates Nos. 59, 60, and 61.
Figure A.5 Infrared Reflectance, Substrates Nos. 63 and 68.
Figure A.6 Infrared Reflectance, Substrates Nos. 70, 71, and 75, before Baking.
Figure A.7  Infrared Reflectance, Substrates Nos. 70, 71, and 75, after Baking for One Hour.
Figure A.8 Infrared Reflectance, Substrates Nos. 71 and 75, after Baking for Two Hours.
APPENDIX B

ENERGY BALANCE CALCULATIONS FOR A FLAT PLATE COLLECTOR

These calculations will evaluate the heat losses and the useful energy available from a typical flat plate collector, first with a non-selective surface. Energy input to the collector is given by

\[ Q_{\text{in}} = I \tau \alpha A \]

where \( I \) is the solar insolation, assumed to be 1000 w/m\(^2\); \( \tau \) is the transmittance of the glass cover plate, 0.9; \( \alpha \) is the absorptance of the collector, 0.95; and \( A \) is the collector area.

\[ Q_{\text{in}} = (1000 \text{ w/m}^2)(0.9)(0.95)(2 \text{ m}^2) = 1710 \text{ watts} \]

The energy loss through insulation on the back of the collector is given by

\[ Q_b = \frac{k}{t} A(T_a - T_p) \quad (3.1) \]

where \( k \) is the thermal conductivity of urethane foam, \( 3.29 \times 10^{-2} \text{ w/m} \cdot \text{°K} \), and \( t \) is the insulation thickness, 0.05 m.
\[ Q_b = \left( \frac{3.29 \times 10^{-2} \text{w/m} \cdot \text{°K}}{0.05 \text{m}} \right)(2 \text{ m}^2)(25^\circ\text{C} - 100^\circ\text{C}) \]

\[ = -98.7 \text{ watts} \]

Heat transfer coefficients for front losses are functions of temperature, so it is necessary to assume a cover temperature, make heat loss calculations, check to see if the heat flow from panel to cover is equal to the heat flow from cover to ambient, and repeat by choosing a new cover temperature. A cover temperature of 40°C will be assumed for the first calculations. Heat transfer from panel to cover by convection:

\[ h_{10} = 1.613 \frac{\Delta T^{0.281}}{0.157} \text{ for horizontal plates} \quad (3.2) \]

\[ h_{10} = (1.613) \frac{(100^\circ\text{C} - 40^\circ\text{C})^{0.281}}{(2.5 \text{ cm})^{0.157}} = 4.414 \text{ w/m}^2 \cdot \text{°K} \]

\[ h_{10} = 1.14 \frac{\Delta T^{0.310}}{0.070} \text{ for tilt angle of 45°} \quad (3.3) \]

\[ h_{10} = (1.14) \frac{(100^\circ\text{C} - 40^\circ\text{C})^{0.310}}{(2.5 \text{ cm})^{0.070}} = 3.804 \text{ w/m}^2 \cdot \text{°K} \]

Interpolating between these values to find \( h_{10} \) for 35°,

\[ h_{10} = 4.278 \text{ w/m}^2 \cdot \text{°K} \]

Correcting for temperature different from 10°C,
\[
\frac{h_{c,p-c}}{h_{10}} = 1 - 0.0018 (\bar{T} - 10) \quad (3.4)
\]

\[\bar{T} = 70°C \]

\[h_{c,p-c} = (4.278 \text{ w/m}^2 \text{ °K})[1 - 0.0018(70 - 10)] = 3.816 \text{ w/m}^2 \text{ °K} \]

Heat transfer by radiation from panel to cover,

\[
h_{r,p-c} = \frac{\sigma(T_p^2 + T_c^2)(T_c + T_p)}{\frac{1}{\varepsilon_p} + \frac{1}{\varepsilon_c} - 1} \quad (3.8)
\]

\[h_{r,p-c} = \frac{(5.6697 \times 10^{-8} \text{ w/m}^2 \text{ °K}^4)[(373\text{°K})^2+(313\text{°K})^2]}{0.95 + 0.88 - 1} \]

\[h_{r,p-c} = 7.719 \text{ w/m}^2 \text{ °K} \]

\[\frac{1}{R_{p-c}} = h_{c,p-c} + h_{r,p-c} = 11.997 \text{ w/m}^2 \text{ °K} \]

The total panel to cover heat transfer resistance is then

\[R_{p-c} = 0.0834 \text{ m}^2 \text{ °K/w} \]

Heat transfer by convection from cover plate,

\[h_{c,c-a} = 5.7 + 3.8 v \quad (3.5)\]
Assuming a wind velocity of 3 m/sec,

\[ h_{c,c-a} = 5.7 + 3.8(3) = 17.10 \text{ w/m}^2 \cdot \text{°K} \]

Heat transfer by radiation from cover plate,

\[ h_{r,c-a} = \frac{\varepsilon c \sigma (T_s^4 - T_c^4)}{T_a - T_c} \tag{3.10} \]

\[ T_s = 0.055(T_a)^{1.5} \]

\[ T_s = 0.055(298\text{°K})^{1.5} = 283\text{°K} \]

\[ h_{r,c-a} = \frac{(0.88)(5.6697\times10^{-8} \text{ w/m}^2 \cdot \text{°K}^4)[(283\text{°K})^4 - (313\text{°K})^4]}{298\text{°K} - 313\text{°K}} \]

\[ h_{r,c-a} = 10.589 \text{ w/m}^2 \cdot \text{°K} \]

The heat transfer resistance from the cover is

\[ \frac{1}{R_{c-a}} = h_{c,c-a} + h_{r,c-a} = 27.89 \text{ w/m}^2 \cdot \text{°K} \]

\[ R_{c-a} = 0.0361 \text{ m}^2 \cdot \text{°K}/\text{w} \]

The total heat flows may now be calculated,

\[ Q_{p-c} = \frac{A(T_c - T_p)}{R_{p-c}} = \frac{(2 \text{ m}^2)(313\text{°K} - 373\text{°K})}{0.0834 \text{ m}^2 \cdot \text{°K}/\text{w}} \]
\[ Q_{p-c} = -1438.8 \text{ watts} \]

\[ Q_{c-a} = \frac{A(T_a - T_c)}{R_{c-a}} = \frac{(2 \text{ m}^2)(298^\circ \text{K} - 313^\circ \text{K})}{0.0361 \text{ m}^2 \text{ }^\circ \text{K/w}} \]

\[ Q_{c-a} = -831.0 \text{ watts} \]

Because \( Q_{p-c} \) is not equal to \( Q_{c-a} \), a new cover temperature must be selected,

\[ \frac{T_c - T_a}{R_{c-a}} = \frac{T_p - T_a}{R_{c-a} + R_{p-c}} \]

\[ \frac{T_c - 298^\circ \text{K}}{0.0361} = \frac{373^\circ \text{K} - 298^\circ \text{K}}{0.0361 + 0.0834} \]

\[ T_c = 320.7^\circ \text{K} \]

Using 48\(^\circ\)C (321\(^\circ\)K) as a second estimate for \( T_c \), and repeating the above calculations, the following results for heat flow are obtained:

\[ Q_{p-c} = -1210.7 \text{ watts} \quad R_{p-c} = 0.0859 \text{ m}^2 \text{ }^\circ \text{K/w} \]

\[ Q_{c-a} = -1207.3 \text{ watts} \quad R_{c-a} = 0.0381 \text{ m}^2 \text{ }^\circ \text{K/w} \]

Because these are within 0.3\%, 48\(^\circ\) will be taken as the cover temperature. Combining resistances for an overall front surface loss gives,

\[ R_F = R_{p-c} + R_{c-a} = 0.0859 + 0.0381 = 0.1240 \text{ m}^2 \text{ }^\circ \text{K/w} \]
\[ Q_F = \frac{A(T_a - T_p)}{R_f} = \frac{(2 \text{ m}^2)(298^\circ \text{K} - 373^\circ \text{K})}{0.1240 \text{ m}^2 \cdot \text{K/w}} \]

\[ Q_F = -1209.7 \text{ watts} \]

The useful energy available is found by an overall balance,

\[ Q_{\text{in}} = Q_{\text{useful}} - Q_F - Q_B \]

\[ Q_{\text{useful}} = 1710 \text{ watts} + (-1209.7 \text{ watts}) + (-98.7 \text{ watts}) \]

\[ Q_{\text{useful}} = 401.6 \text{ watts} \]

This amount of energy is then equivalent to a collector efficiency of

\[ \eta_c = \left(\frac{401.6 \text{ watts}}{1710 \text{ watts}}\right)(100\%) = 23.5\% \]

An overall efficiency can also be calculated,

\[ \eta_o = \left(\frac{401.6 \text{ watts}}{2000 \text{ watts}}\right)(100\%) = 20.1\% \]

This system will now be reanalyzed by assuming the collector to have a selective surface with \( \varepsilon = 0.05 \). Other conditions will remain the same. Energy input and back losses will remain the same:

\[ Q_{\text{in}} = 1710 \text{ watts} \]

\[ Q_B = -98.7 \text{ watts} \]
A cover temperature of 40°C will again be assumed for the first calculations. Heat transfer from the panel to the cover will not be changed, so

\[
h_{c,p-c} = 3.816 \text{ w/m}^2 \text{ °K}
\]

Heat transfer from panel to cover by radiation,

\[
h_{r,p-c} = \frac{(5.6697 \times 10^{-8} \text{ w/m}^2 \text{ °K}^4) [(373^\circ \text{K})^2 + (313^\circ \text{K})^2]}{\frac{1}{0.05} + \frac{1}{0.88} - 1}
\]

\[
h_{r,p-c} = 0.458 \text{ w/m}^2 \text{ °K}
\]

\[
\frac{1}{R_{p-c}} = 3.816 \text{ w/m}^2 \text{ °K} + 0.458 \text{ w/m}^2 \text{ °K} = 4.274 \text{ w/m}^2 \text{ °K}
\]

\[
R_{p-c} = 0.234 \text{ m}^2 \text{ °K/w}
\]

Heat transfer by radiation and convection from the cover plate will be the same as originally calculated, so

\[
h_{c,c-a} = 17.10 \text{ w/m}^2 \text{ °K}
\]

\[
h_{r,c-a} = 10.589 \text{ w/m}^2 \text{ °K}
\]

\[
R_{c-a} = 0.0361 \text{ m}^2 \text{ °K/w}
\]

Calculating the heat flows,
\[ Q_{p-c} = \frac{(2 \text{ m}^2)(313^\circ K - 373^\circ K)}{0.234 \text{ m}^2 \circ K/\text{w}} = -493.8 \text{ watts} \]

\[ Q_{c-a} = \frac{(2 \text{ m}^2)(298^\circ K - 313^\circ K)}{0.0361 \text{ m}^2 \circ K/\text{w}} = -831.0 \text{ watts} \]

It is again necessary to find a new estimate for the cover temperature,

\[ \frac{T_c - 298^\circ K}{0.0361} = \frac{373^\circ K - 298^\circ K}{0.0361 + 0.234} \]

\[ T_c = 308.0 ^\circ K \]

The following results are obtained using 35°C (308°K) as a second estimate for \( T_c \) and repeating the calculations:

\[ Q_{p-c} = -567.7 \text{ watts} \]
\[ R_{p-c} = 0.229 \text{ m}^2 \circ K/\text{w} \]

\[ Q_{c-a} = -600.6 \text{ watts} \]
\[ R_{c-a} = 0.0333 \text{ m}^2 \circ K/\text{w} \]

This is not close enough yet, so another value for \( T_c \) will be tried,

\[ \frac{T_c - 298^\circ K}{0.0333} = \frac{373^\circ K - 298^\circ K}{0.0333 + 0.229} \]

\[ T_c = 307.5 ^\circ K \]

Again repeating the calculations for \( T_c = 34.5^\circ C \),

\[ Q_{p-c} = -574.1 \text{ watts} \]
\[ R_{p-c} = 0.2282 \text{ m}^2 \circ K/\text{w} \]
These answers are close enough, so a cover temperature of $34.5^\circ C$ is assumed to be correct. Again combining resistances for an overall front surface loss gives

$$R_F = 0.0329 + 0.2282 = 0.2611 \text{ m}^2 \cdot \text{°K/w}$$

$$Q_F = \frac{(2 \text{ m}^2)(298°K - 373°K)}{0.2611 \text{ m}^2 \cdot \text{°K/w}} = -574.5 \text{ watts}$$

$$Q_{useful} = 1710 \text{ watts} - 574.5 \text{ watts} - 98.7 \text{ watts}$$

$$Q_{useful} = 1036.8 \text{ watts}$$

This useful energy in turn gives collector and overall efficiencies of

$$\eta_c = \left( \frac{1036.8 \text{ watts}}{1710 \text{ watts}} \right)(100\%) = 60.6\%$$

$$\eta_o = \left( \frac{1036.8 \text{ watts}}{2000 \text{ watts}} \right)(100\%) = 51.8\%$$
APPENDIX C

REFLECTANCE CALCULATIONS FOR THIN FILMS

The effect of a film of aluminum oxide on the net reflectance of aluminum may be calculated using the equations of Section 3.2. Brannon and Goldstein (1970) give the following data for optical properties as functions of wavelength:

<table>
<thead>
<tr>
<th>Wavelength (μm)</th>
<th>( n_f )</th>
<th>( k_f )</th>
<th>( n_2 )</th>
<th>( k_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>1.57</td>
<td>0.00</td>
<td>2.30</td>
<td>16.5</td>
</tr>
<tr>
<td>5</td>
<td>1.49</td>
<td>0.00</td>
<td>7.10</td>
<td>33.02</td>
</tr>
<tr>
<td>10</td>
<td>1.31</td>
<td>0.088</td>
<td>20.18</td>
<td>57.33</td>
</tr>
</tbody>
</table>

At a wavelength of 2 μm and assuming \( n_1(\text{air}) = 1 \),

\[
g_1 = \frac{1 - (1.57)^2 - (0.00)^2}{(1 + 1.57)^2 + (0.00)^2} = -0.2218
\]

\[
g_2 = \frac{(1.57)^2 - (2.30)^2 - (0.00)^2 - (16.5)^2}{(1.57 + 2.30)^2 + (0.00 + 16.5)^2} = -0.9577
\]

\[
h_1 = \frac{(2)(1)(0.00)}{(1 + 1.57)^2 + (0.00)^2} = 0.00
\]
\[ h_2 = \frac{2[(1.57)(16.5) - (2.30)(0.00)]}{(1.57 + 2.30)^2 + (0.00 + 16.5)^2} = 0.1804 \]

\[ A = 2[(-0.2218)(-0.9577) + (0.00)(0.1804)] = 0.4248 \]

\[ B = 2[(-0.2218)(0.1804) - (0.9577)(0.00)] = -0.0800 \]

\[ D = 2[(-0.2218)(0.1804) + (0.9577)(0.00)] = -0.0800 \]

\[ E = 2[(-0.2218)(-0.9577) - (0.00)(0.1804)] = 0.4248 \]

Assuming a film thickness \( d_f = 50 \text{ Å} = 5.0 \times 10^{-3} \text{ µm} \),

\[ \mu_1 = \frac{2(0.00)(5.0 \times 10^{-3} \text{ µm})}{2 \text{ µm}} = 0.00 \]

\[ \gamma_1 = \frac{2(1.57)(5.0 \times 10^{-3} \text{ µm})}{2 \text{ µm}} = 0.0247 \]

\[ R = \frac{\left\{ (-0.2218)^2(1) + [(-0.9577)^2 + (0.1804)^2](1) \right\} + (0.4248) \cos 2(0.0247) + (-0.0800) \sin 2(0.0247)}{1 + (-0.2218)^2[(-0.9577)^2 + (0.1804)^2] + (0.4248) \cos 2(0.0247) + (-0.0800) \sin 2(0.0247)} \]

\[ R = 0.9674 \]

By similar calculations, the reflectance may be found for other wavelengths and film thicknesses, with the results given in Table C.1.
Table C.1. Calculated Reflectance of Aluminum with a Thin Film of Aluminum Oxide.

<table>
<thead>
<tr>
<th>Film Thickness (Å)</th>
<th>Wavelength</th>
<th>2.0 µm</th>
<th>5.0 µm</th>
<th>10.0 µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.9675</td>
<td>0.9754</td>
<td>0.9783</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.9675</td>
<td>0.9754</td>
<td>0.9782</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.9674</td>
<td>0.9754</td>
<td>0.9776</td>
<td></td>
</tr>
</tbody>
</table>

The net reflectance of a selective surface of chromium oxide on aluminum may also be calculated with the above procedure. The following data for optical properties as functions of wavelength are from Hahn (1976) for chromium oxide and from Hellwege and Hellwege (1962) for aluminum. The results of these calculations are given in Table C.2 and Figures 3.4 and 3.5:

<table>
<thead>
<tr>
<th>Wavelength (µm)</th>
<th>Cr₂O₃</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n_f</td>
<td>k_f</td>
</tr>
<tr>
<td>0.65</td>
<td>2.07</td>
<td>0.021</td>
</tr>
<tr>
<td>0.90</td>
<td>2.00</td>
<td>0.028</td>
</tr>
<tr>
<td>2.00</td>
<td>1.96</td>
<td>0.016</td>
</tr>
</tbody>
</table>
Table C.2 Calculated Reflectance of a Chromium Oxide on Aluminum Selective Surface.

<table>
<thead>
<tr>
<th>Film Thickness (µm)</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.65 µm</td>
</tr>
<tr>
<td>0.00</td>
<td>0.8979</td>
</tr>
<tr>
<td>0.01</td>
<td>0.8841</td>
</tr>
<tr>
<td>0.02</td>
<td>0.8590</td>
</tr>
<tr>
<td>0.03</td>
<td>0.8164</td>
</tr>
<tr>
<td>0.04</td>
<td>0.7496</td>
</tr>
<tr>
<td>0.05</td>
<td>0.6580</td>
</tr>
<tr>
<td>0.06</td>
<td>0.5817</td>
</tr>
<tr>
<td>0.07</td>
<td>0.5724</td>
</tr>
<tr>
<td>0.08</td>
<td>0.6303</td>
</tr>
<tr>
<td>0.09</td>
<td>0.7034</td>
</tr>
<tr>
<td>0.10</td>
<td>0.7623</td>
</tr>
<tr>
<td>0.11</td>
<td>0.8030</td>
</tr>
<tr>
<td>0.12</td>
<td>0.8292</td>
</tr>
<tr>
<td>0.13</td>
<td>0.8443</td>
</tr>
<tr>
<td>0.14</td>
<td>0.8504</td>
</tr>
<tr>
<td>0.15</td>
<td>0.8481</td>
</tr>
<tr>
<td>0.16</td>
<td>0.8363</td>
</tr>
<tr>
<td>0.17</td>
<td>0.8124</td>
</tr>
<tr>
<td>0.18</td>
<td>0.7712</td>
</tr>
<tr>
<td>0.19</td>
<td>0.7057</td>
</tr>
<tr>
<td>0.20</td>
<td>0.6110</td>
</tr>
<tr>
<td>0.21</td>
<td>0.5023</td>
</tr>
<tr>
<td>0.22</td>
<td>0.4352</td>
</tr>
<tr>
<td>0.23</td>
<td>0.4596</td>
</tr>
<tr>
<td>0.24</td>
<td>0.5452</td>
</tr>
<tr>
<td>0.25</td>
<td>0.6346</td>
</tr>
</tbody>
</table>
APPENDIX D

SPRAY COATING DISTRIBUTION CALCULATIONS

The film coating distribution may be found using equation 3.41,

\[ d_F = \frac{N_0 V_d C_s}{\pi z^2} \frac{M_{Cr_2O_3}}{M_{Cr-Nitrate}} \frac{t}{\rho_{Cr_2O_3}} e^{-r^2/z^2} \]

The droplet volume, \( V_d \), is found by using an average droplet size of 1.0 \( \mu \) (1.0 x 10^{-4} \text{ cm}) and assuming that the droplets are spherical,

\[ V_d = \frac{\pi d^3}{6} = \frac{\pi}{6} (1.0 \times 10^{-4} \text{ cm})^3 = 5.236 \times 10^{-13} \text{ cm}^3 \]

The total droplet flow rate, \( N_0 \), is found by dividing the volumetric flow rate by the droplet volume,

\[ N_0 = \frac{(1.0 \text{ cm}^3/\text{min})(1 \text{ min}/60 \text{ sec})}{5.236 \times 10^{-13} \text{ cm}^3/\text{droplet}} = 3.183 \times 10^{10} \text{ droplets/sec} \]

This assumes a flow rate of 1.0 cm³/min. A concentration of chromium nitrate in the solution of 0.010 g/cm³ will also be assumed. The reaction stoichiometry gives a molecular weight ratio of 0.18992. The density of chromium oxide is 5.21 g/cm³ (Weast 1967, p. B-169). For a spraying time of 10.0 min, the distribution equation becomes,
\[
\begin{align*}
    d_f &= \frac{3.183 \times 10^{10}}{\sec} \frac{5.23 \times 10^{-13}}{\pi} \frac{\text{cm}^3}{0.010 \text{ g}} \frac{0.18992}{0.18992} \frac{600.0 \text{ sec}}{5.21 \text{ g/cm}^3} e^{-r^2/z^2} \\
    d_f &= \frac{1.160 \times 10^{-3}}{z^2} \frac{\text{cm}^3}{e^{-r^2/z^2}} \\
\end{align*}
\]

Assuming a distance of 8.0 cm from nozzle to substrate,

\[
    d_f = 1.813 \times 10^{-5} \text{ cm} e^{-r^2/64.0 \text{ cm}^2}
\]

At the center of the substrate, \( r = 0 \), the thickness should be 1.813 \( \times 10^{-5} \) cm or 1813 Å. At the edge of a 6.0 cm square substrate, \( r = 3.0 \) cm,

\[
    d_f = 1.813 \times 10^{-5} \text{ cm} e^{-9.0 \text{ cm}^2/64.0 \text{ cm}^2}
\]

\[
    d_f = 1.575 \times 10^{-5} \text{ cm} = 1575 \text{ Å}
\]

At a corner of the square, \( r = 4.243 \) cm,

\[
    d_f = 1.813 \times 10^{-5} \text{ cm} e^{-18.0 \text{ cm}^2/64.0 \text{ cm}^2}
\]

\[
    d_f = 1.369 \times 10^{-5} \text{ cm} = 1369 \text{ Å}
\]

To find the average film thickness, the distribution function may be integrated over the area, and then divided by the area. For the
integration, a radius which gives an area equal to that of the square plate:

\[ r_m = \sqrt{\frac{36.0 \, \text{cm}^2}{\pi}} = 3.385 \, \text{cm} \]

\[ d_{fm} = \frac{(1.160 \times 10^{-3} \, \text{cm}^3)(2\pi)}{36.0 \, \text{cm}^2} \left[ -e^{-r^2/z^2} \right]_0^{3.385 \, \text{cm}} \]

\[ d_{fm} = (1.012 \times 10^{-4} \, \text{cm}^3)[-e^{-r^2/z^2}]_0^{3.385 \, \text{cm}} \]

\[ d_{fm} = 1.659 \times 10^5 \, \text{cm} = 1659 \, \text{Å} \]

The theoretical efficiency may be calculated by integrating the droplet flux density at the same limits, multiplying by droplet volume and time, and comparing with the total volume sprayed:

\[ V = 2 V_d t \int_0^{3.385 \, \text{cm}} \frac{N_o}{\pi z^2} re^{-r^2/z^2} \, dr \]

\[ V = V_d t N_o \int_0^{3.385 \, \text{cm}} \frac{2r}{z^2} e^{-r^2/z^2} \, dr \]

\[ V = 5.236 \times 10^{-13} \, \text{cm}^3 \frac{3.183 \times 10^{10} \, \text{droplet}}{\text{sec}} \frac{600.0 \, \text{sec}}{\text{sec}} \]

\[ \left[ -e^{-r^2/64.0 \, \text{cm}^2} \right]_0^{3.385 \, \text{cm}} \]

\[ V = 1.639 \, \text{cm}^3 \]
$$V_r = (1.0 \text{ cm/min})(10.0 \text{ min}) = 10.0 \text{ cm}$$

$$\text{Eff.} = \frac{1.639 \text{ cm}^3}{10.0 \text{ cm}} \times 100\% = 16.4\%$$
APPENDIX E

CALCULATIONS OF ELECTROSTATIC EFFECT

The theoretical efficiency of electrostatic spraying may be calculated with the equations in Section 3.5. To solve equation 3.64 for efficiency, it is first necessary to find the precipitating velocity in equation 3.60,

\[ w = \frac{2p \varepsilon_E E_0 a}{3 \mu} \]

In this equation,

\[ p = 2\left( \frac{\kappa_p - 1}{\kappa_p + 2} \right) + 1 \]

where the particle dielectric constant, \( \kappa_p \), should be approximately equal to that of water:

\[ \kappa_p = 80.36 \text{ at } 20^\circ\text{C} \quad \text{(Weast 1967, p. E-65)} \]

\[ p = 2\left( \frac{80.36 - 1}{80.36 + 2} \right) + 1 = 2.927 \]

\[ \varepsilon_o = 8.85 \times 10^{-12} \text{ F/m} \]

For the experimental apparatus, at a voltage of 12.0 kV across a distance of 4.0 cm,
\[ E_c' = E_p = 3.00 \times 10^5 \text{ V/m} \]

For particles of 1 \( \mu \text{m} \) diameter,

\[ a = 5.0 \times 10^{-7} \text{ m} \]

The viscosity of air at 20°C is

\[ \mu = 183.40 \times 10^{-6} \text{ g/cm sec} \quad \text{(Weast 1967, p. F-41)} \]

\[ w = \frac{2}{3} \frac{2.927 \times 8.85 \times 10^{-12} \text{ F coul.} \cdot (3.00 \times 10^5 \text{ V/m})^2 \cdot 5.0 \times 10^{-7} \text{ m}}{183.40 \times 10^{-6} \text{ g} \cdot \text{V-coul.} \cdot 1.000 \times 10^7 \text{ g-cm}^2 \cdot 1.000 \times 10^4 \text{ cm}^2} \]

\[ w = 4.237 \text{ cm/sec} \]

Because the particles are very small, the Cunningham correction factor should be calculated to determine whether it will significantly affect the velocity. To find the mean free path, \( \lambda \), it is first necessary to find the molecular volume from the molecular density,

\[ \rho_m = \frac{6.0222 \times 10^{23} \text{ molecules}}{22.400 \text{ cm}^3} \text{ at } 0^\circ \text{C, 760 mm Hg} \]

\[ \rho_m = \frac{2.6885 \times 10^{19} \text{ molecules}}{\text{cm}^3} \text{ at } 273^\circ \text{K, 700 mm Hg} \]

\[ \rho_m = \frac{2.3072 \times 10^{19} \text{ molecules/cm}^3} \text{ at } 293^\circ \text{K, 760 mm Hg} \]
\[ V_m = 4.3342 \times 10^{-20} \text{ cm}^3 \]

\[ \lambda = \frac{3}{V_m} = 3.5127 \times 10^{-7} \text{ cm} = 3.5127 \times 10^{-9} \text{ m} \]

\[ C = 1 + \frac{3.5127 \times 10^{-9} \text{ m}}{5.0 \times 10^{-7} \text{ m}} \left\{ 1.26 + 0.400 \exp \left[ - \frac{(1.10)(3.5727 \times 10^{-9} \text{ m})}{5.0 \times 10^{-3} \text{ m}} \right] \right\} \]

\[ C = 1.012 \]

This correction factor is then small enough to be safely ignored.

To check the assumption of laminar particle movement, which was used in the derivation of equation 3.60, a particle Reynolds number may be calculated by equation 3.58:

\[ \text{Re} = \frac{\rho \cdot g \cdot w(2a)}{\mu} \]

\[ \rho_g = 1.2929 \text{ g/l at } 0^\circ \text{C, 760 mm Hg} \quad \text{(Weast 1967, p. A-10)} \]

Correcting for temperature and pressure,

\[ \rho_g = \frac{1.2929 \text{ g/l}}{1000 \text{ cm}^3} \frac{273^\circ \text{K}}{293^\circ \text{K}} \frac{700 \text{ mm Hg}}{760 \text{ mm Hg}} \]

\[ \rho_g = 1.1095 \times 10^{-3} \text{ g/cm}^3 \]

\[ \text{Re} = \frac{1.1095 \times 10^{-3} \text{ g/cm}^3 \times 4.237 \text{ cm} \times 1.0 \times 10^{-4} \text{ cm}}{183.4 \times 10^{-6} \text{ g cm-sec}} \]

\[ \text{Re} = 0.0026 \]
This value is well within the range for laminar flow, so it is appropriate to use equation 3.60. Using substrates 6.0 cm on a side, the total collection area will be

$$A' = (6.0 \text{ cm})^2 = 36.0 \text{ cm}^2$$

The Sonicore nozzle operating at 44 psig uses 1.1 scfm of air,

$$V_g = \frac{1.1 \text{ ft}^3}{\text{min}} \times \frac{28.320 \text{ cm}^3}{1 \text{ ft}^3} \times \frac{1 \text{ min}}{60 \text{ sec}} \times \frac{293^\circ \text{K}}{273^\circ \text{K}} \times \frac{760 \text{ mm Hg}}{700 \text{ mm Hg}}$$

$$V_g = 605.0 \text{ cm}^3/\text{sec}$$

Finally, the efficiency may be calculated with equation 3.64,

$$\eta = 1 - e^{-A'w/V_g}$$

$$\eta = 1 - \exp\left[-\frac{(36.0 \text{ cm}^2)(4.237 \text{ cm/sec})}{605.0 \text{ cm}^3/\text{sec}}\right] = 0.223$$

This efficiency may be improved by increasing the strength of the electric field. At a field strength of $6.00 \times 10^5 \text{ V/m}$,

$$w = 16.949 \text{ cm/sec}$$

$$\eta = 0.635$$

At a field strength of $8.00 \times 10^5 \text{ V/m}$,

$$w = 30.132 \text{ cm/sec}$$
These efficiencies are only for the electrostatic part of the apparatus. To find an overall efficiency, it is necessary to use distribution calculations like those in Appendix D to find the fraction of the spray which may be affected by the electrostatic field. For example, if the discharge electrode is a screen, 15.0 cm square, mounted perpendicular to the spray and a distance of 8.0 cm from the nozzle, with a solution flow rate of 1.0 cm³/min, then only 67.3% of the droplets will impinge on the screen to become charged. This in turn leads to overall efficiencies of 15.0% at a field strength of 3.00 x 10⁵ V/m, 42.7% at 6.00 x 10⁵ V/m, and 56.1% at 8.0 x 10⁵ V/m.
**LIST OF SYMBOLS**

### Upper Case

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>A</td>
<td>Solar energy collector area (equation 3.1)</td>
</tr>
<tr>
<td>A</td>
<td>A function of $g_1$, $g_2$, $h_1$, and $h_2$ (equation 3.23)</td>
</tr>
<tr>
<td>A'</td>
<td>Cumulative collection area (equation 3.63)</td>
</tr>
<tr>
<td>B</td>
<td>A function of $g_1$, $g_2$, $h_1$, and $h_2$ (equation 3.23)</td>
</tr>
<tr>
<td>C</td>
<td>Cunningham correction factor (equation 3.61)</td>
</tr>
<tr>
<td>$C_D$</td>
<td>Dimensionless drag coefficient (equation 3.57)</td>
</tr>
<tr>
<td>$C_p$</td>
<td>Uniform particle concentration (equation 3.63)</td>
</tr>
<tr>
<td>$C_s$</td>
<td>Solution concentration (equation 3.43)</td>
</tr>
<tr>
<td>D</td>
<td>A function of $g_1$, $g_2$, $h_1$, and $h_2$ (equation 3.23)</td>
</tr>
<tr>
<td>$D_o$</td>
<td>Frequency factor for diffusion (equation 3.34)</td>
</tr>
<tr>
<td>$D_T$</td>
<td>Diffusivity at temperature $T$ (equation 3.34)</td>
</tr>
<tr>
<td>E</td>
<td>A function of $g_1$, $g_2$, $h_1$, and $h_2$ (equation 3.23)</td>
</tr>
<tr>
<td>$E'_c$</td>
<td>Charging electrostatic field (equation 3.60)</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Radial component of electrostatic field (equation 3.48)</td>
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<tr>
<td>$E_o$</td>
<td>Electrostatic field strength (equation 3.48)</td>
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<tr>
<td>$E_p$</td>
<td>Precipitating electrostatic field (equation 3.60)</td>
</tr>
<tr>
<td>F</td>
<td>Drag force on a particle (equation 3.57)</td>
</tr>
<tr>
<td>$F_{1-2}$</td>
<td>Shape factor relating two surfaces (equation 3.6)</td>
</tr>
<tr>
<td>L</td>
<td>Spacing between cover plate and collector (equation 3.2)</td>
</tr>
<tr>
<td>M</td>
<td>Molecular weight (equation 3.43)</td>
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<td>N</td>
<td>Spray droplet flux density (equation 3.37)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<td>--------</td>
<td>------------------------------------------------------------------------------</td>
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<tr>
<td>N</td>
<td>Ion cloud density</td>
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<tr>
<td>N&lt;sub&gt;max&lt;/sub&gt;</td>
<td>Maximum droplet flux density</td>
</tr>
<tr>
<td>N&lt;sub&gt;o&lt;/sub&gt;</td>
<td>Overall droplet flow rate</td>
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<tr>
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<td>Ion density</td>
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<tr>
<td>Q</td>
<td>Activation energy</td>
</tr>
<tr>
<td>Q&lt;sub&gt;b&lt;/sub&gt;</td>
<td>Uniform surface charge on particle</td>
</tr>
<tr>
<td>Q&lt;sub&gt;r&lt;/sub&gt;</td>
<td>Heat loss rate from back of collector</td>
</tr>
<tr>
<td>Q&lt;sub&gt;r&lt;/sub&gt;</td>
<td>Radiant heat transfer rate</td>
</tr>
<tr>
<td>R</td>
<td>Reflectance</td>
</tr>
<tr>
<td>R&lt;sub&gt;Re&lt;/sub&gt;</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>R&lt;sub&gt;Re&lt;/sub&gt;</td>
<td>Reynold's number</td>
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<tr>
<td>T&lt;sub&gt;A&lt;/sub&gt;</td>
<td>Average temperature</td>
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<tr>
<td>T&lt;sub&gt;a&lt;/sub&gt;</td>
<td>Ambient temperature</td>
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<td>T&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Cover plate temperature</td>
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<tr>
<td>T&lt;sub&gt;p&lt;/sub&gt;</td>
<td>Collector plate temperature</td>
</tr>
<tr>
<td>T&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Effective sky temperature</td>
</tr>
<tr>
<td>U</td>
<td>Potential energy of an ion due to its position in a field</td>
</tr>
<tr>
<td>V</td>
<td>Total solution volume impinging on a substrate</td>
</tr>
<tr>
<td>V&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Electrostatic voltage</td>
</tr>
<tr>
<td>V&lt;sub&gt;d&lt;/sub&gt;</td>
<td>Spray droplet volume</td>
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<tr>
<td>V&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Volumetric gas velocity</td>
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**Lower Case**

a | Particle radius | 3.48 |
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<th></th>
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<tbody>
<tr>
<td>a&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Constant</td>
<td>3.37</td>
</tr>
</tbody>
</table>
$a_2$  Constant (equation 3.38)
$b$  Ion mobility (equation 3.51)
$c$  Concentration of diffusing species (equation 3.35)
$d_F$  Thickness of thin film (equation 3.20)
$g_1$  Function of complex refractive indices (equation 3.23)
$g_2$  Function of complex refractive indices (equation 3.23)
$h_1$  Function of complex refractive indices (equation 3.23)
$h_2$  Function of complex refractive indices (equation 3.23)
$h_{10}$  Heat transfer coefficient at $10^\circ C$ (equation 3.2)
$h_r$  Radiant heat transfer coefficient (equation 3.8)
$h_T$  Heat transfer coefficient at temperature $T$ (equation 3.4)
$h_{\text{wind}}$  Convection heat transfer coefficient (equation 3.5)
$k$  Thermal conductivity (equation 3.1)
$k$  Extinction index (equation 3.24)
$k$  Boltzmann's constant (equation 3.52)
$k_A$  Precipitator constant (equation 3.62)
$n$  Index of refraction (equation 3.15)
$p$  Function of $\kappa_p$ (equation 3.49)
$q$  Ionic charge (equation 3.51)
$r$  Reflection coefficient (equation 3.17)
$r$  Radial distance from nozzle centerline (equation 3.37)
$r$  Radial distance from particle (equation 3.48)
$r_\pi$  Reflection coefficient for radiation parallel to plane of incidence (equation 3.15)
Reflection coefficient for radiation perpendicular to plane of incidence (equation 3.16)

Thickness of insulation (equation 3.1)

Time (equation 3.35)

Wind velocity (equation 3.5)

Root mean square ion velocity (equation 3.54)

Particle migration velocity (equation 3.57)

Linear position (equation 3.35)

Axial distance from nozzle (equation 3.38)

Absorptance (equation 3.12)

Function of thin film thickness and refractive index (equation 3.23)

Function of thin film thickness and refractive index (equation 3.19)

Emittance (equation 3.6)

Free space permittivity (equation 3.48)

Precipitation efficiency (equation 3.62)

Angle of refracted radiation (equation 3.15)

Polar angle between \( r \) and \( E_0 \) (equation 3.48)

Particle relative dielectric constant (equation 3.48)

Wavelength of radiation (equation 3.12)

Mean free path of gas molecules (equation 3.61)

Gas viscosity (equation 3.58)
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<th>Symbol</th>
<th>Description</th>
<th>Equation</th>
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<tbody>
<tr>
<td>$\mu_1$</td>
<td>Function of thin film thickness and extinction index</td>
<td>3.23</td>
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<td>$\rho$</td>
<td>Reflectance</td>
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<tr>
<td>$\rho$</td>
<td>Bulk density</td>
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<tr>
<td>$\rho_g$</td>
<td>Gas density</td>
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<td>$\sigma$</td>
<td>Stefan-Boltzmann constant</td>
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<td>$\tau$</td>
<td>Particle charging time constant</td>
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</tr>
<tr>
<td>$\phi$</td>
<td>Angle of incident radiation</td>
<td>3.15</td>
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</tbody>
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REFERENCES


