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ANTI-REFLECTION COATINGS APPLIED BY ACID LEACHING PROCESS

FINAL REPORT
MOTOROLA REPORT NO. 2370/4
DRD NO. SE-5

SEPTEMBER 1980

JPL CONTRACT NO. 955387

PREPARED BY

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THE JPL LOW-COST SOLAR ARRAY PROJECT IS SPONSORED BY THE U.S. DEPARTMENT OF ENERGY AND FORMS PART OF THE SOLAR PHOTOVOLTAIC CONVERSION PROGRAM TO INITIATE A MAJOR EFFORT TOWARD THE DEVELOPMENT OF LOW-COST SOLAR ARRAYS. THIS WORK WAS PERFORMED FOR THE JET PROPULSION LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY BY AGREEMENT BETWEEN NASA AND DOE.

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ABSTRACT

The Magicote C process developed by S.M. Thompsen was evaluated for use in applying an antireflective coating to the cover plates of solar panels. The process uses a fluosilicic acid solution supersaturated with silica at elevated temperature to selectively attack the surface of soda-lime glass cover plates and alter the physical and chemical composition of a thin layer of glass. The altered glass layer constitutes an antireflective coating.

The process produces coatings of excellent optical quality which possess outstanding resistance to soiling and staining. The coatings produced are not resistant to mechanical abrasion and are attacked to some extent by glass cleansers. Control of the filming process was found to be difficult.

1.0 SUMMARY

In 1951 the details of a simple method for producing antireflective (AR) coatings were published. The process, known as Magicote C, was intended to be used on optical components but was soon replaced by vacuum deposition methods and fell into disuse.

The increasing level of manufacture of solar modules with their large glass cover plates revived interest in the Magicote process as a possibly effective method of treating large area coverplates so as to increase their transmission of light to increase power production and reduce glare.

The process was evaluated on the basis of: process control, abrasion resistance, chemical resistance, stain and soil resistance, and the effect of process variations on optical performance.

Optical efficiency was found to be particularly good, with peak transmission of 99.8% achieved in the visible spectrum on low-iron glass. Soil and stain resistance were also excellent, being essentially the same as for unfilmed glass.

Resistance to chemical attack by common glass cleansers was fair. It was also found that filmed glass was easily damaged by abrasion, with the highly transmissive films being more readily damaged than those of lower optical quality produced by the same method.

Production of antireflective film is accomplished by immersion of soda-lime glass sheets in an inherently unstable liquid fluosilicic acid solution at elevated temperature. Only at certain compositions of the acid solution is film produced, and extended use of the acid solution entails frequent trial-and-error adjustment of chemical composition to maintain a working process.

Difficult process control and low abrasion resistance lead to the conclusion that the process is not acceptable for present use on cover panels of photovoltaic solar modules.

2.0 INTRODUCTION

The use of glass or plastic cover materials for photovoltaic modules is a necessity imposed by the need to protect underlying photovoltaic cells from the damaging effects of weather, atmosphereic constitutents, and other environmental factors. In addition to the need for durability, solar modules are required to be efficient, so that the cost per unit power produced is low enough to permit their widespread application. The use of any cover material reduces the efficiency of a module by reflecting some of the incident light away from the module, reducing the amount available for absorption by the enclosed solar cells.

The loss of light by reflection is a consequence of the fact that all solid substances which can be used as cover materials possess refractive indices higher than that of air. From elementary optical theory, it can be shown that the amount of light reflected by a material-air interface is described by

$$R = \left(\frac{n_o - n_c}{n_o + n_c}\right)^2 \qquad (1)$$

where

R = fraction of light reflected

n_o = refractive index of air $\approx$ 1.0

n_c = refractive index of cover material

For glass and plastic, the two materials most often employed as covers, n_c is approximately 1.5. Therefore, about four percent of the light incident on the module is lost by reflection from the front surface of the cover. If the bottom glass surface interfaces with air, four percent of the remaining light is lost by reflection from the rear surface and the cover -- a combined loss of nearly eight percent, even if the cover material is perfectly clean and transparent. In flat plate modules, reflection of light from the rear surface of the cover is reduced (or eliminated) by the use of an organic encapsulant placed between the cells and the cover glass and in contact with both. If the refractive index of the organic encapsulant is equal to that of the cover, no reflective loss is suffered. Although this technique is widely applied, reflective loss from the front surface of the cover still results. Moreover, the use of an inner encapsulant is impractical for some applications such as concentrator collectors, where large enclosed volumes would require large amounts of encapsulant, creating problems of excessive weight and optical absorption, and complicating the problem of heat dissipation. In both cases, reduction of glare from the outer surface will be another consequential feature of antireflective treatment.

A technique for use in reducing reflection from surfaces is known and has been practiced for some time in the optical industry. If a thin film of transparent material is placed in contact with a surface such as glass, reflection of light may be reduced by means of proper choice of film thickness and refractive index.

The film used can, in theory, extinguish reflection of light of any desired wavelength. Moreover, reflection of light at neighboring wavelengths is strongly attenuated. The following equations define the requirements of a film that extinguishes surface reflection.

$$n_f = \sqrt{n_c} \qquad (2)$$

$$n_f d_f = \frac{1}{4} \lambda \qquad (3)$$

where

n_f = refractive index of the film

n_c = refractive index of the cover material

d_f = thickness of the film

λ = wavelength of incident light.

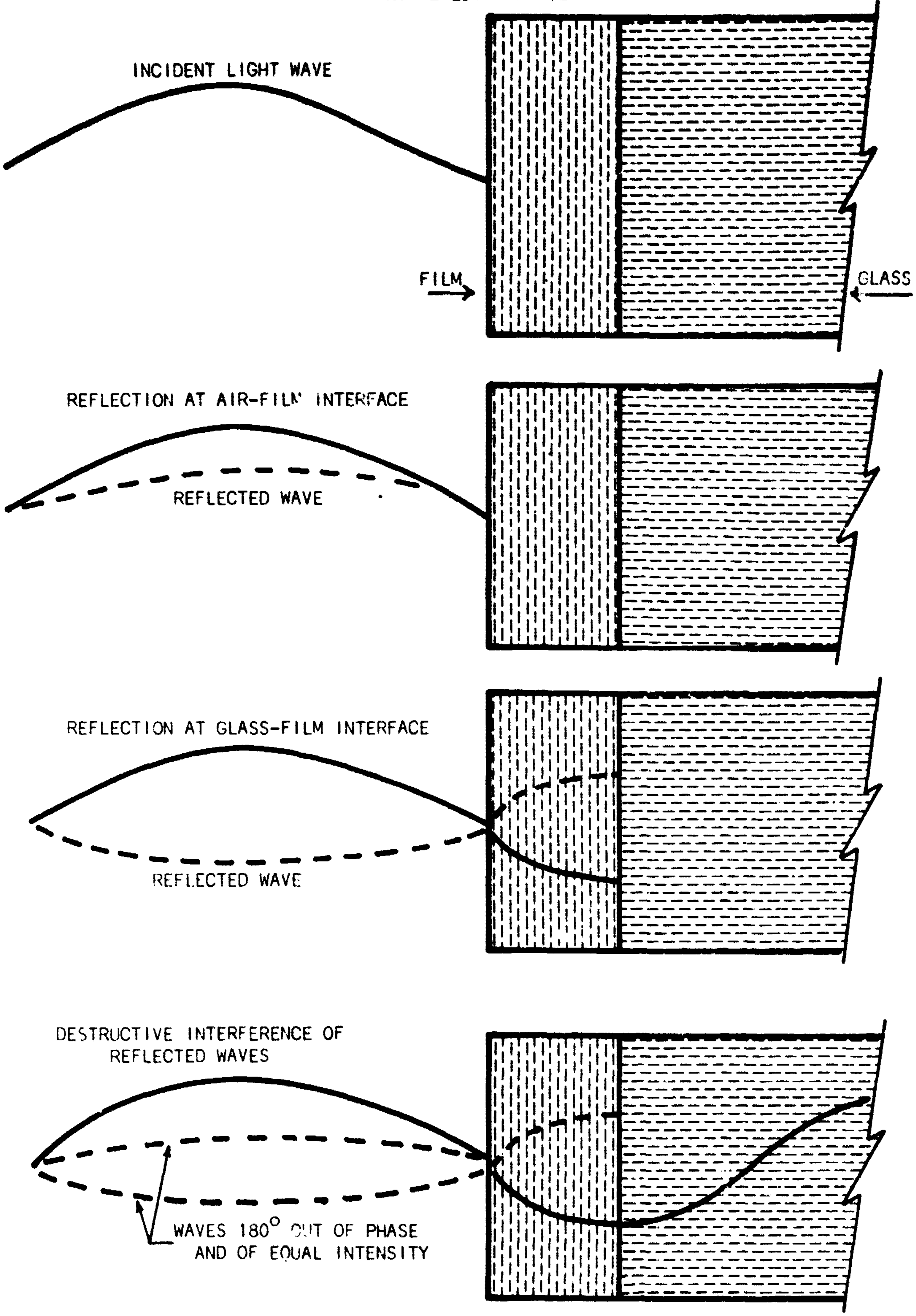
Unfortunately, the refractive index of a film that will extinguish reflection on soda-lime glass and most plastics is about 1.225, a value that is possessed by few solid substances. Microporous films can closely approach (or attain) the optimum value, and some solid substances, such as magnesium fluoride, have indexes low enough to permit substantial reflection reduction.

The physics of reflection reduction by thin films requires extensive mathematical development in order to be rigorously reviewed and is beyond the scope of this report. Details of the theory may be found in textbooks on optics. A somewhat simplified presentation will suffice to illustrate the principles involved.

For the sake of simplicity, assume that a wave of monochromatic light of wavelength λ impinges on a glass surface coated with a thin film having the properties described in equations 2 and 3. The wave approaches perpendicular to the surfaces and a portion of it is reflected from the front surface of the film, undergoing phase reversal in the process. The remainder of the light traverses the film and after traveling one-quarter wavelength strikes the film-glass interface. Again a portion of the light is reflected and undergoes phase reversal. The remaining light passes into the glass and is transmitted. That part of the light reflected at the film-glass interface will be of the same intensity as that reflected at the air-film interface if the film's refractive index is equal to $\sqrt{n_{glass}}$. The wave reflected at the film-glass interface again traverses the film and emerges at the air-film interface. Since both reflected waves have undergone phase reversal, the net difference between them is now one-half wavelength (having crossed a film of ¼d thickness twice, one of the waves is one half wavelength out of phase with the other). Being of equal intensity, the two reflected waves interfere destructively and cancel each other so that no light is reflected. Therefore, no reflection loss occurs and complete transmission of light into the glass is achieved. (Although this type of explanation is accepted as accurate, it does lead to the philosophical question "how does the wave reflected at the air-film surface know that another wave is subsequently going to be reflected at the film-glass interface and destructively interfere with it?") Figure 1 illustrates the process schematically.

The production of antireflective films in the optical industry is routinely done by the evaporation of a material of low refractive index onto optical surfaces in a high vacuum. While this technique is successful, it is not well suited to the coating of large, flat pieces of material, such as module cover sheets. Evaporation techniques characteristically deposit thicker coatings of material on areas nearer the evaporator source, so that the arrangement of objects to be coated is usually in the form of a sphere, with every part of every object approximately the same distance from the source. Large planar panels cannot be conveniently adapted for use in such evaporators. The alternative is the use of moving evaporator sources which travel around the object to be coated, thereby producing an even coating. These moving sources are expensive, as is all of the equipment associated with evaporation, while the necessity of preserving a vacuum during coating operations slows the process and further increases cost. For use with low cost solar modules, a different approach to the formation of antireflective coatings must be taken.

FIGURE 1
THEORY OF ANTIREFLECTIVE FILMS



3.0 TECHNICAL DISCUSSION

3.1 THE ACID ETCHING PROCESS

One way of producing an antireflective film on glass in a relatively inexpensive way is to avoid depositing the film at all, but rather, to transform a layer of glass at the surface to a form such that the refractive index and thickness of the layer are suitable for use as an antireflective agent. This may be done by treating the glass with reagents that selectively remove certain glass components, such as calcium and sodium, while leaving constituents such as silicon dioxide unaffected. This treatment results in a layer at the glass surface that consists of a "skeleton" of interlocking silica molecules, which is microscopically porous owing to the absence of the removed calcium and sodium ions. This silica layer possesses a lower refractive index than silica in other forms, for instance, quartz, because of its porous structure. The degree of porosity, and hence the refractive index, can be controlled by regulating the vigor of attack on the calcium and sodium ions, or by formulating the etching reagent so that the silica itself is attacked and removed to some extent, thus increasing porosity beyond what would be possible if calcium and sodium alone were removed. The thickness of the silica layer can also be adjusted to an optimum value by adjusting the duration of etching.

The etching process was developed and refined before and during World War II in an effort to provide a means of meeting requirements for high quality optical instruments at a time when the art of vacuum deposition of AR films was in the early stages of development and was still impractical for large scale use. The first application of this technique used hydrofluoric acid vapor as the etchant (1). Later, the use of fluosilicic acid vapor was reported (2). The development of a liquid etch reagent proceeded more slowly, and after many two- or three-stage processes involving the use of mineral acids were disclosed, details of methods using fluosilicic acid supersaturated with silica were published (3,4). After the development of efficient evaporation techniques for producing AR coatings on optical components, the etching techniques received no serious consideration from the optical industry and the processes appear to have been abandoned.

Perhaps the most advanced etching technique was devised by S.M. Thompsen. The method was detailed in a patent (reference 4), already cited, and was later published, in more readable form, in the RCA Review (5). Unlike the present vacuum deposition techniques, Thompsen's method is applicable to very large and/or irregularly shaped surfaces, requires very simple process equipment, and is inexpensive.

The process described by Thompsen in reference 5 was adapted for use in our experiments in order to evaluate the suitability of AR treated glass for use as solar module covers.

The etch consists of 1.25 molar fluosilicic acid (H_2SiF_6) in aqueous solution. The solution is saturated with silica by the addition of finely divided silica or hydrated silica, sometimes referred to as "silicic acid". An etch of this composition will dissolve the calcium and sodium ions from glass, but will dissolve the silica as well, forming no AR coating. The dissolution of silica can be reduced by supersaturating the fluosilicic acid with silica by the addition of boric acid. The degree of supersaturation is critical, affecting the refractive index of the AR coating formed, and the speed of attack on glass. Moreover, the degree of supersaturation determines whether or not the glass will film at all. Different formulations of soda lime glass, and even different lots of the same formulation of glass, may require different degrees of supersaturation which must be controlled to a fairly high degree of accuracy to assure that filming will occur. The control of the supersaturation is made more difficult because the supersaturated solution spontaneously reverts to saturated form by precipitating excess silica, making readjustment of the etchant necessary by the periodic addition of boric acid.

The time required to produce an AR coating on glass varies with the temperature of the etch. Although the process will work with an etch used at room temperature, filming takes hours to occur. In order to shorten processing time, Thompsen recommends a temperature of 45°C, and states that at further elevated temperatures, processing proceeds even more quickly. For the purposes of this project, etching was conducted primarily at 45°C for the production of test samples of AR coated glass for optical and durability tests. Limited experiments in etching at 55°C and 65°C were done to evaluate the possiblity of high-speed processing, without subjecting the samples produced to durability tests.

3.2 EXPERIMENTAL PROCEDURE

3.2.1 CHOICE OF GLASS

Inasmuch of the nature of the glass affects the results obtained, efforts were made to limit glass variations. For this investigation, the glass used was low-iron Lustraglass, a soda-lime glass manufactured by ASG Industries, Inc. The low-iron content of the glass was desirable in that the presence of iron increases light absorption and imparts a green color to glass that affects the results of optical measurements. The Lustraglass used still displayed a green tint when viewed on-edge, but the color was much less pronounced than that which is seen in ordinary glass, such as that used for windows. All glass was 2.5 mm in thickness and was cut from large sheets of the same lot into 4 inch square plates to permit ease of handling.

3.2.2 PREPARATION OF GLASS

Glass typically acquires substantial amounts of dust, grit, and oil on its surface, and develops a chemically altered "weathered" outer layer during packing, shipping, and storage. This contamination has adverse effects on both the quality of the AR coating produced during etching and the stability of the etchant bath itself. Therefore, cleaning of the glass is necessary to prepare for AR coating.

Glass was prepared for filming by a wash and etch sequence. Glass received from the manufacturer was first rinsed briefly in water to remove dust and gross surface contamination. The glass was then submerged for thirty minutes in a boiling solution consisting of 12 ml of Joy dishwashing detergent per liter of deionized water. (Physical abrasion of the glass surface was not employed.) After a brief rinse to remove detergent, the glass was etched for 1 min. in 10% by volume concentrated hydrofluoric acid in water to remove the weathered layer. The glass was then rinsed in deionized water, and wiped dry with paper towels. At this point, glass was ready for immediate insertion into a prepared AR etch bath.

3.2.3. PREPARATION OF THE BATH

As obtained from the supplier, fluosilicic acid was in the form of a 23% aqueous solution. To prepare the 1.25 molar solution required, 670 ml of the commercial acid was diluted to a volume of 1.0 liter with deionized water. The solution was raised to its operating temperature (typically 45°C, but on occasion 55°C or 65°C) and 30 grams of 200 - 300 mesh silica in the form of silicic acid was added per liter of etch. The resulting slurry was agitated continuously overnight at temperature, then filtered through paper to remove undissolved silica. The filtered solution was then stored at room temperature in polyethylene bottles until use. Cooling of the silica-saturated etch to room temperature resulted in no precipitation of silica. Experience gained in operation of the etch solution suggested that the solubility of silica in the fluosilicic acid solution was decreased at elevated temperatures. At the time of use, the solution was returned to the temperature at which it was saturated.

3.2.4 USE OF THE BATH

3.2.4.1 EQUIPMENT

Although Thompsen states that the etch solution may be stored and used in vessels of Pyrex borosilicate glass, early attempts at using Pyrex containers resulted in a roughening of the glass or the development of hazy gray patches on surfaces of the glass which were in contact with the etch bath. While it could not be demonstrated that this effect harmed the performance of the etch bath or seriously damaged the vessel, it was felt that greater control over the bath composition could be realized by the use of vessels composed of more inert materials. Therefore polyethylene containers were used in our experiments.

The facility used for filming glass consisted of a large hot plate equipped with a magnetic-coupled stirrer and a thermistor temperature probe. On the hot plate was placed a stainless-steel basin filled with water. The thermistor probe permitted control of the water temperature to within ±1°C. Into the water basin was placed a 2 quart polyethylene container with a tightly fitting snap-on lid. The etch solution was kept in the polyethylene container and continuously agitated by means of a teflon coated magnetic stirring pellet driven by the hot plate. Plates of glass to be AR treated were loaded into a polypropylene photomask holder which held ten 10 cm (4 inch) square plates at a time. The holder and plates were lowered into the etch solution, the cover was placed on the vessel, and etching took place unattended. After etching, the holder and plates were withdrawn, placed into a box, and rinsed in briskly flowing deionized water for ten minutes. Afterward, the plates were rinsed in isopropyl alcohol and then dried by exposure to hot freon fumes in a vapor degreaser. In this way, drying was accomplished without wiping or otherwise abrading the surfaces of the treated glass.

3.2.4.2 ADJUSTMENT OF THE BATH

The silica-saturated fluosilicic acid solution described in section 3.2.3 attacks glass very slowly, but produces no AR effect. Further adjustment of solution composition is necessary to obtain the desired effect; specifically, the solution must be made supersaturated with silica. The concept of supersaturation (and the degree of supersaturation) is made more easily understood by defining the term "potency".

Potency, as described by Thompsen, relates to the vigor of the solution's attack on the glass. A solution of 1.25M aqueous fluosilicic acid saturated with silica is assigned an arbitrary potency value of zero. The potency increases as the solution is made less than saturated. This can be accomplished, for instance, by the addition of hydrofluoric acid to the solution. One unit increase in potency is defined as that change in saturation caused by the addition of one millimole of HF per liter of solution. If, for convenience, 3M potassium fluoride in aqueous solution is used in place of HF, the addition of one milliliter of KF solution to one liter of filming solution will result in two units' increase in potency. In order to produce a solution that films glass, the potency must be made negative, that is, supersaturation must be effected. A 4% by weight aqueous solution of boric acid is used. The addition of one milliliter of boric acid solution to one liter of filming solution causes a decrease of two potency units.

The potency of a solution that successfully films glass depends strongly on the chemical composition of the glass and typically varies for different brands of glass and even for different lots of the same glass. There is no way of determining, by knowledge of glass composition alone, the proper potency of the solution to be used. For this reason, an empirical method of determining proper potency is used.

In our experiments, approximately 1.8 liters of zero potency filming solution was brought to operating temperature in the polyethylene vessel described in section 3.2.4.1. Series of plastic test tubes were placed into the temperature controlled water vessel; the tubes were filled with 5 ml of filming solution from the vessel and to each tube was added enough of a very dilute boric acid solution to produce a series of test-tube size samples of filming solutions differing from each other by one or two potency units. Into each tube was placed a small sliver cut from a sheet of glass. The tubes were then stoppered and allowed to stand for 30 to 60 minutes. Examination of the glass slivers after etching identified the active potency (or range of potencies), and the solution in the polyethylene container was then adjusted to the active potency value. Etching of 10 cm square glass samples was then undertaken. Successful filming was found to occur in solutions of from -18.3 to -20.5 potency. Specific details about the effects of potency on filming will be presented in section 3.3.5 -- Process Variations.

3.2.4.3 MAINTENANCE OF THE BATH

The control of bath composition is essential to maintaining a working process. Although bath temperature is easily maintained, control of bath potency presents problems. Since the etch produces AR films only when supersaturated with silica, the problems are compounded by the fact that supersaturated solutions are inherently unstable. They tend to spontaneously revert to saturated solutions by the precipitation of solute. During use, silica was rejected from solution in every bath prepared for use. Curiously, and in contrast to previous experience, the precipitated silica did not appear in a dense form that sank to the bottom of the solution, but rather occurred in the form of a fine buoyant powder that floated on top of the liquid, and as a granular form that appeared and grew on the sides of the vessel at the liquid meniscus. The precipitation of silica of course led to a decrease in the degree of supersaturation so that boric acid solution had to be added daily (or even more often) in order to maintain an effective potency level. The amount of boric acid to be added was determined by the test tube trials described in the previous section.

Precipitation of silicon dioxide from the bath was unexpectedly large, inasmuch as the original reference suggested filtration once a month. It was found necessary to filter the bath at least once every two days; daily filtration was often necessary. The speed of potency drift was also found to be greater than expected. At times, the bath had a useful life of one or two hours before addition of boric acid was necessary to restore it. Filtration of the bath helped in reducing the speed of degeneration. By employing daily filtering, daily change to HF-cleaned etch vessels, and daily replenishment of evaporated solution, as well as use of an air-tight cover, low rates of degeneration were found, amounting to a need for approximately 2 ml of 4% H_3BO_3 to be added per liter of filming solution per day. Even so, frequent test tube trials were necessary to determine when fine adjustments of supersaturation were needed.

3.3 INVESTIGATIONS AND RESULTS

Samples of filmed glass used in the tests described in this section were all produced, unless otherwise noted, at 45°C. The duration of etch was variable, being extended or shortened by trial and error techniques so as to produce films of a uniform purple appearance when viewed with reflected light by the unaided eye. Potency values also varied slightly, but were always close to -18.5. The intent was to produce, by expedient means, a large supply of filmed glass samples for testing. Out of the over 300 samples produced, those with the best antireflection characteristics, as determined by unaided human observation, were chosen for testing.

3.3.1 BATH CONTROL

Earlier work (6) on this method of producing antireflective films indicated that control of the bath composition was central to the establishment of a practical process yielding reproducible results. This indication was once again borne out by the experience gained from work on this project.

The time required for etching an antireflective layer to a particular thickness is a function of both etch temperature and potency, with potency being by far the more difficult condition to control. Control of thickness is important in that it allows the manufacturer to "tune" the film to permit maximum transmission of a certain range of wavelengths. Thus the transmission of the cover glass can be adjusted to take advantage of, for example, the solar spectrum peak or the wavelengths to which the enclosed photovoltaic cells are most sensitive. In addition, the potency of the solution also determines the refractive index of the film and hence its optical effectiveness. Aside from these considerations of the quality of an AR film, the fact must be recognized that at most potency values the etch simply doesn't work.

Thompsen gives no information about determining the proper potency for use with glass of a known chemical composition by a purely analytical technique. Similarly, determination of the amount of boric acid addition needed to restore an etch to working potency by analytical technique alone is, at present, not possible. In both cases, recourse to test tube trials is necessary.

If the etch process were to be used on a large scale in industry, some more convenient method of potency testing would have to be found. Since only one glass composition was used for this project, correlation of glass chemistry variations with successful potency values could not be attempted. Some effort was exerted in trying to find a convenient method of monitoring and controlling potency drift however. Thompsen, in a separate article (7), describes methods of fluosilicic acid analysis by titration and other methods. The titration method of analyzing silica content of the AR etch was tried, without success. In addition to being as time-consuming and as much trouble to perform as test tube trials, the analytical technique was not sensitive enough to detect potency drift with any acceptable degree of accuracy. Other methods of analysis, including determination of density, viscosity, surface tension, pH, spectral absorption, and fluoride ion concentration by specific ion electrode techniques, also failed to yield useful information. A practical method of analysis has yet to be found.

3.3.2 PHYSICAL ABRASION

Because the anti reflective coating produced by the acid etch technique is composed of microporous silica, it was reasonable to suspect that the coating would be more susceptible to damage from physical abrasion than untreated glass. The durability of the coating is important because the production of the AR film entails an additional expense in the manufacture of a solar module, and the film must remain on the module long enough to pay back its cost by enhancing power output. Unfortunately, the forces of nature conspire against anything that is intended to be durable. Rain, hail, blowing dust, and freezing moisture are among the abrasive forces to which solar modules are exposed.

During production of samples for testing, it was found that very heavy pressure exerted on the film by a fingernail was sufficient to damage the film. Attempts to employ the eraser rub test specified in Military Specification MIL-C-675A for testing of AR coatings on optical elements were unsuccessful, owing to the fact that only one stroke of the specified rubber-pumice eraser removed all film. Even trying a soft and non-abrasive vinyl drafting eraser produced film removal, apparently because of the adhesive nature of the rubber or vinyl ingredients. However, the samples did withstand a tape test, in which cellophane adhesive tape pressed tightly to the filmed surface was withdrawn, both slowly and quickly. Given these conflicting results, a different abrasion test was arranged to provide quantitative data on film strength.

Two samples of filmed glass having a transmission of 99.8% at 460 µm were chosen as the primary objects of the test. It was felt that abrasion resistance may have been dependent on film porosity, which controls antireflective performance. In order to test this assumption, five samples each of two less optically efficient antireflective-filmed samples were also tested. All samples were filmed at 45°C.

Abrasion was performed in two ways: without abrasive by a cotton pad, and with the same cotton pad loaded with abrasive powder. The pad was composed of 4 layers of .023 cm (0.009 inch) thick cotton duck, with a circular area of 13.9 cm^2. The pad was loaded with weights to yield a pressure of 138 g/cm^2. After conducting abrasion tests with the pad on samples of filmed glass, the pad was stamped in Buehler No. 40-6475 AB, 3200 mesh abrasive, then tapped to remove adhering clumps of abrasive so that only the abrasive that had been worked into the cloth was available. The abrasive on the pad was renewed for each of the five samples tested. The testing was performed by moving the pad laterally across the filmed glass surface in 5 cm (2 inch) strokes, with visual inspection of the glass after every few strokes. A sample was tested with the plain cotton pad and with the pad and abrasive in five places. The results are summarized below.

STROKES REQUIRED TO DAMAGE FILMED SAMPLES

TEST FILMS

⟶ INCREASING TRANSMISSION

ABRASIVE	EFFECT	ACID ETCHED #1	ACID ETCHED #2	ACID ETCHED #3 99.8% TRANSMISSION
CLOTH ONLY	First sign of damage	80	30	20
	Moderate damage	200	100	50
CLOTH PLUS ABRASIVE	First sign of damage	20	1	1
	Moderate damage	200	40	20
	Film Removed	>300	200	150

As shown by the results, increasing antireflective effectiveness does adversely affect abrasion resistance. It may be pointed out that in no case was film removal possible without an abrasive powder; only moderate damage could be achieved. Moderate damage was defined as unmistakable damage covering the entire stroked area but not resulting in complete removal of film from any area. With the abrasive powder, damage of all types was inflicted easily on the two most antireflective samples. The least antireflective sample was the most rugged; the ">300" strokes required for film removal caused 95% of the film to be removed from the stroked area, since complete removal appeared impossible. With the other films, removal was complete. Although these results appear discouraging, it may be pointed out that the powdered abrasive test was unusually severe. Even samples of lacquered metal surfaces sustained what would be classified as moderate damage after 30 strokes.

3.3.3 CHEMICAL RESISTANCE

3.3.3.1 FUME EXPOSURE

Inasmuch as AR filmed module covers will be exposed to atmospheric pollutants during their lives, exposure to acid and other fumes was performed in order to assess the damage, if any, caused by gaseous atmospheric contaminants. The following fumes were generated in airtight containers, and samples of filmed glass were enclosed in the containers for one week at room temperature. Samples were rinsed and dried after exposure, then evaluated.

FUME	EFFECT ON FILM
Ammonia, dry	none
Carbon dioxide, dry	none
Hydrogen chloride, wet	none

Nitric acid vapor, wet	none
Nitrogen, dry (control)	none
Nitrogen dioxide, dry	slight brown stain; washed out with water.
Sulfur dioxide, dry	none

3.3.3.2 CLEANING AGENTS

The effects of cleaning agents likely to be used on solar module covers were evaluated. Continuous exposures of 7 days and 30 days were conducted at room temperature, without agitation of the cleansers or wiping of the glass. After exposure, the samples were rinsed in deionized water and air dried before evaluation. Unless otherwise stated, all cleansers were in undiluted form.

CLEANING AGENT	7 DAY EXPOSURE	30 DAY EXPOSURE
Deionized water	no effect	no effect
Tap water	no effect	no effect
Joy Detergent (0.5 volume % in tap water)	no effect	no effect
Isopropyl alcohol	no effect	no effect
Parson's clear ammonia	no effect	some removal of film
Windex	slight change in color of film	removal of film
Fantastic Spray Cleaner	removal of film	removal of film

Despite the fact that the AR film is composed of highly inert silica, it still suffered attack from the high pH cleansers. In fact, Fantastic was the most vigorous in its attack. Although a quick dip and rinse with this cleaner caused

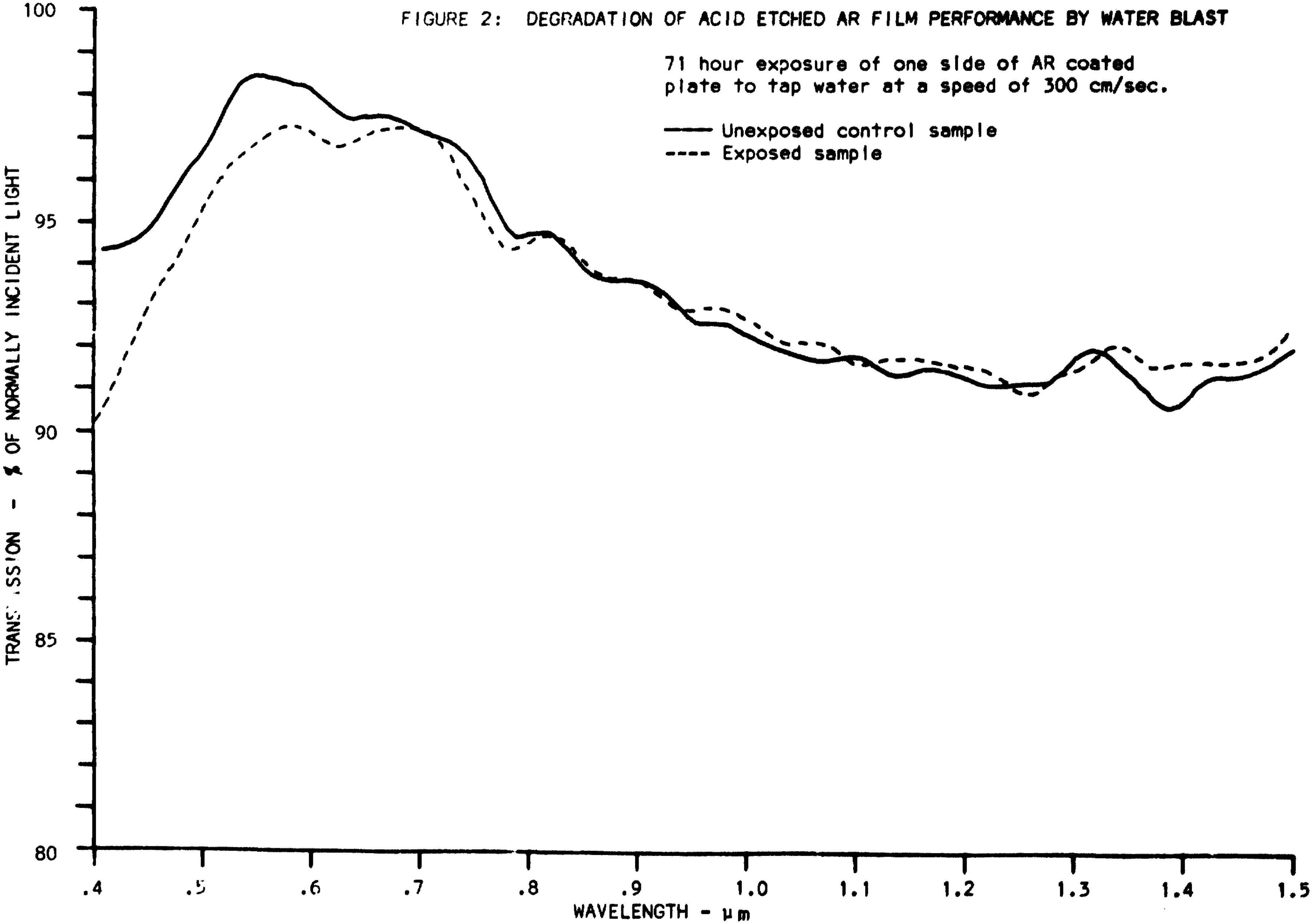


FIGURE 2: DEGRADATION OF ACID ETCHED AR FILM PERFORMANCE BY WATER BLAST

71 hour exposure of one side of AR coated plate to tap water at a speed of 300 cm/sec.

no discernable damage, an exposure of only ten minutes' duration removed the film from samples. Although the product label cautions against use on glass, Fantastic is a good grease remover, and it was felt that products like it might be used occasionally. In addition, even Windex and household ammonia had damaging effects, and these were designed specifically for glass.

3.3.3.3 WATER BLAST

In order to simulate the exposure to heavy rain or an occasional cleaning with a spray from a garden hose that filmed module covers might face, a water blast was performed. In this test, a stream of rapidly moving tap water was directed downward at a filmed glass sample, striking the sample perpendicular to its surface. The water stream had a circular cross section with a diameter of 13 millimeters and a velocity of approximately 300 cm/sec. The water blast was sustained continuously for 71 hours. The water blast exposure caused a slight decrease in transmission in the short wavelengths of the visible spectrum. (Figure 2).

3.3.4 STAIN AND SOIL RESISTANCE

Being mounted out-of-doors, solar modules are exposed to an array of stains and soils, particularly those of biological origin. Actual two week outdoor exposure of samples under conditions prevailing in Phoenix, Arizona produced no detectable change in film properties other than the acquisition of a fine layer of dust which was quickly rinsed away with water. Optical efficiency was not affected. Since the exposure resulted in no biological staining, it was decided to simulate staining and soiling in the laboratory and then attempt removal.

3.3.4.1 STAINS

Several stains were prepared by dissolving various dyes and pigments in solvents to form saturated solutions (except in the case of India ink, which was used as received). The solutions were applied to separate areas of of the same glass samples and baked at 60°C for two hours to dry and set the stains, then removal of stains was attempted by a sequence of successively more drastic cleaning steps in the following order:

1. rinsing for ten minutes in water
2. gentle wiping with a soft paper towel in water
3. soaking for ten minutes in 0.5% Joy solution, wiping with a paper towel, and rinsing
4. wiping with rubbing alcohol and rinsing.

The nature of the stains, and the least drastic cleaning step required to remove each stain, are listed below.

STAIN	CLEANING REQUIRED
Aniline Blue in water	Rinsed off with water
Brilliant Green in acetone	All but traces rinsed off with water Removal of last traces required alcohol wipe.
Cresol Red in isopropyl alcohol	Rinsed off with water
Crystal Violet in acetone	All but traces rinsed off Last traces removed by wiping with water
India Ink	Wiped off with water
Sodium Fluorescein in water	Rinsed off with water
Sudan IV in acetone	Wiped off with alcohol

It is significant that untreated glass required identical cleaning methods in every case. Insofar as resistance to staining is concerned, AR filmed glass is equivalent to unfilmed glass.

3.3.4.2 SOILS

In order to test the film's ability to release sticky soils, the following substances were deposited on separate areas of the same sample plates:

1. corn syrup
2. egg
3. evaporated milk
4. mucilage
5. peanut butter
6. brown paste shoe polish

These substances were chosen as being representative of greasy, proteinaceous, and highly adherent components present in biological soiling agents. The sample plates were then baked at 60°C for two hours, drying all of the soiling substances except the peanut butter into hard, adherent plaques.

The plates were immersed in a 0.5% by volume solution of Joy dishwashing detergent and gently wiped with a soft paper towel. All substances except the shoe polish were removed. Removal of shoe polish was effected only by use of an organic solvent such as methylene chloride. Identical results were obtained with unfilmed glass plates, so soil resistance of acid etch AR filmed glass is the same as that of unfilmed glass.

3.3.4.3 SOOT

Because soot is a common atmospheric pollutant, and because of its opaque nature, module covers must be able to shed soot easily. This is a particular concern with acid etched films because their microporous nature suggests that they may trap and hold tiny soot particles.

Soot was deposited on filmed glass samples and on bare glass samples by exposing the samples to a turpentine flame. It was found, without exception, that rinsing with vigorously flowing water removed soot completely from the filmed glass samples. The same treatment invariably left minor traces of soot on the bare glass samples.

3.3.4.4 FINGERPRINTS

Fingerprints severly affect acid etched AR coatings because the microscopic pores absorb and hold the moisture, oils, and salts present, thus raising the refractive index of the film and lowering its antireflective effectiveness.

Freshly applied fingerprints posed no serious problems, since these could be removed with a detergent-water solution and gentle wiping. When fingerprints were allowed to remain on the film for 24 hours or longer, removal became impossible with detergent solutions; only the use of rubbing alcohol or acetone followed by a water rinse was effective.

3.3.5 PROCESS VARIATIONS AND OPTICAL EFFECTIVENESS

3.3.5.1 POTENCY EFFECTS

As described earlier, only solutions with certain potency values will film glass. At 45°C, filming occurred in solutions having a range of potencies from -18.3 to -19.5. Within this range, the AR effectiveness of films produced was fairly equal. Minor variations outside of this range severely effected filming. For example, at -18.0 no filming occurred. At -20, filming occurred only on a few sheets of glass out of a batch of ten sheets etched at the same time in the same etch solution. Those sheets that did etch had films of very poor AR effectiveness; the presence of film was difficult to detect at all. Figure 3 shows a plot of spectral transmissions of films etched at potencies of -18.3, -18.5, -19, and -19.5. The plots also show the high transmissions of the filmed samples compared to the transmission of an unfilmed sample.

An interesting (and as yet unreported) effect was noted during production of the acid etched films -- solution potency profoundly effects filming time even when temperature is held constant. Reference to Figure 3 shows that the transmission characteristics are fairly similar, yet the times required to produce the films varied as follows:

SOLUTION POTENCY	ETCH TIME
-18.3	97 minutes
-18.5	120 minutes
-19.0	133 minutes
-19.5	136 minutes

Such variation in required etch times in a solution of intrinsic potency instability would cause process control problems in production.

3.3.5.2 TEMPERATURE EFFECTS

As expected, increased temperature of the etching bath significantly reduced etching time required to produce film of a given transmission. Figure 4 shows the transmissions of films produced at 45°C, 55°C, and 65°C, along with the etch times used.

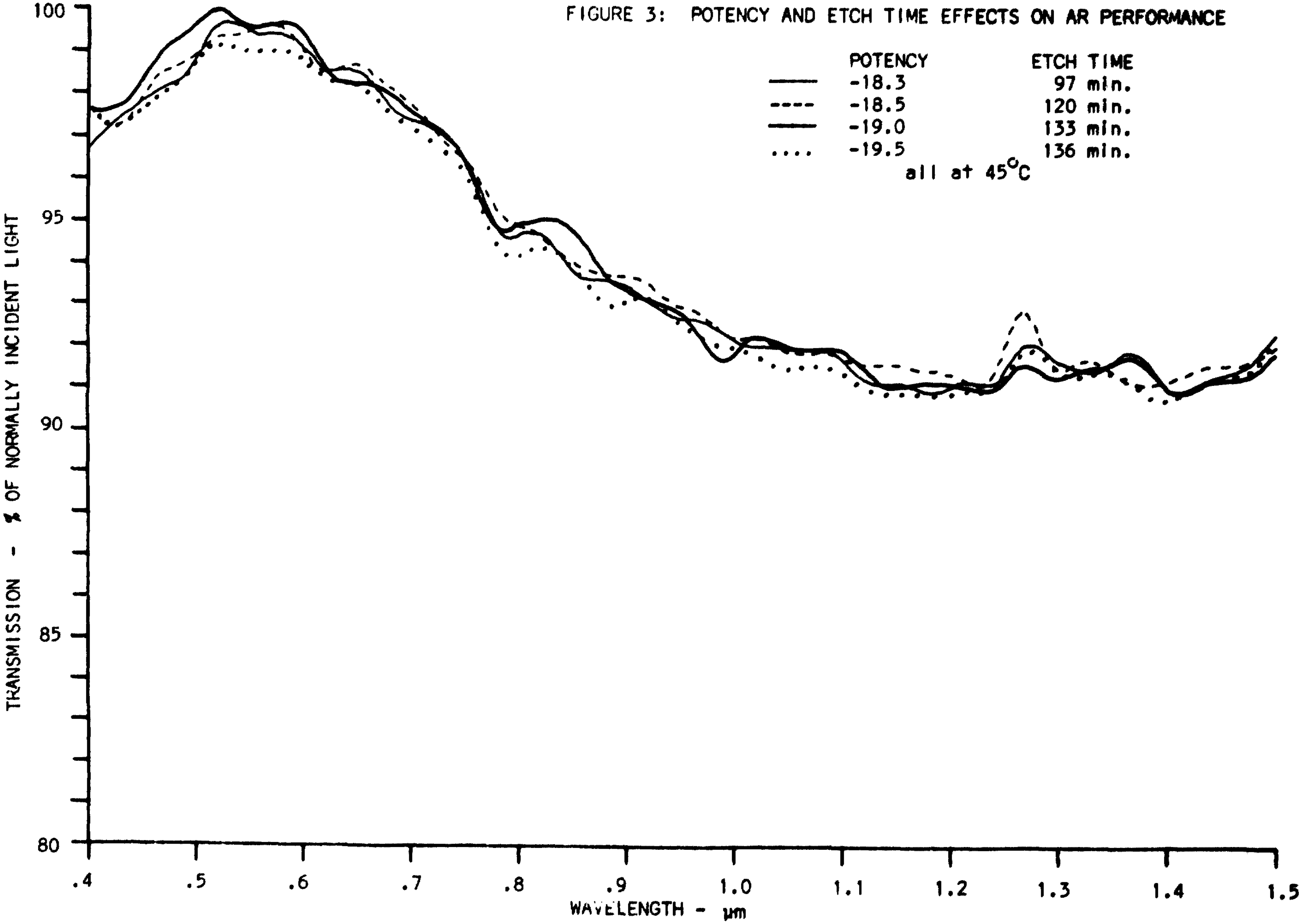


FIGURE 3: POTENCY AND ETCH TIME EFFECTS ON AR PERFORMANCE

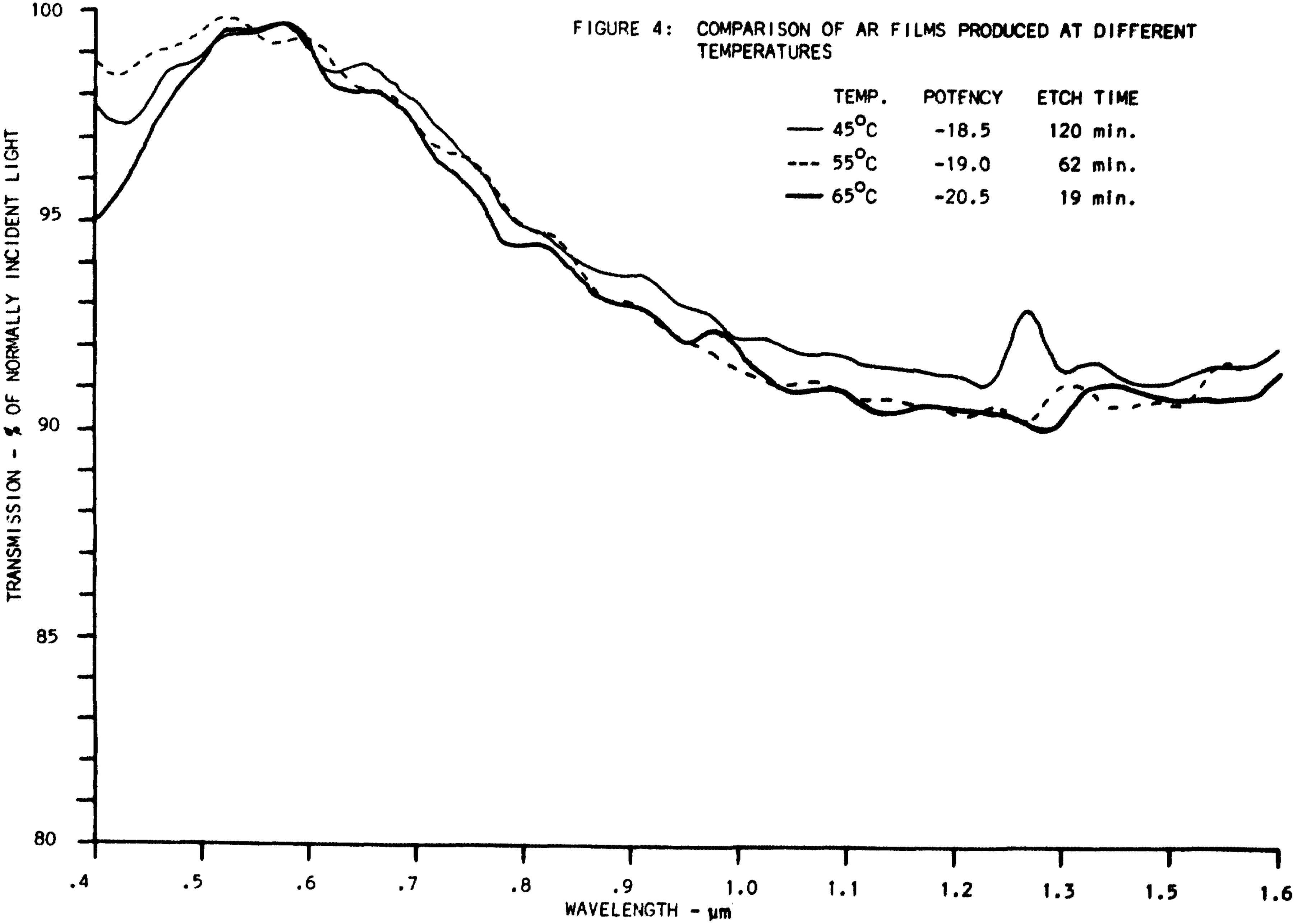


FIGURE 4: COMPARISON OF AR FILMS PRODUCED AT DIFFERENT TEMPERATURES

Aside from the reduction of etch duration permitted by higher temperatures, other effects were noted. Preparation of saturated silica-fluosilicic acid mixtures took longer at 55°C and 65°C than at 45°C. At 65°C, for example, 48 to 72 hours of continuous agitation was necessary to ensure saturation of the solution, compared with the 16 hours required at 45°C.

As temperature was increased, a slight shift in successful potency values was noted. While potencies of -18.3 to -19.5 produced films at 45°C, potencies of -19 to -19.5 were successful at 55°C, and potencies of -19.5 to -20.5 were necessary to film at 65°C. No explanation has been advanced for this effect other than that, even with the prolonged mixing times allowed for the silica-fluosilicic acid mixtures at 55 and 65°C, complete saturation of the fluosilicic acid solution may not have occurred. If this were the case, a lower apparent potency would have to be used in order to compensate for the slightly unsaturated nature of the starting fluosilicic acid solution.

A third additional temperature effect was discovered -- filmed samples prepared at elevated temperatures had less consistent film thickness than those prepared at lower temperatures. The inconsistency was noted as variations in the color of the film as viewed by reflected light. This effect may be due to the fact that the very short processing times used at high temperatures simply do not allow the average etch rates on different areas of the glass surface to approach each other. Any inconsistencies in the glass surface that delay the onset or slow the rate of etching in certain areas are magnified by the fact that the time spent etching slowly or not at all may be a significant fraction of the etch cycle. The slow areas, in effect, never have a chance to catch up.

3.3.5.3 TIME EFFECTS

The effect of variations in etch time is to shift the wavelength of light that is least reflected by varying the thickness of the film. Etching glass samples for successively longer periods of time results in samples whose peak transmissions are at successively longer wavelengths. Figure 5 illustrates this by showing transmission data for two films produced under conditions that were identical except for etch time.

3.3.5.4 POTENTIAL OF THE PROCESS

The potential for production of high optical quality AR films exists with the acid etch process. Figure 6 is a plot of the transmission of the best film obtained, demonstrating a 99.8% peak transmission. The AM2 solar spectrum is also plotted, to an arbitrary scale, showing that the peak transmission is near to the solar spectrum peak. A plot of unfilmed glass transmission is also included for comparison.

It is significant to note that, outstanding as this performance is, only twenty filmed samples out of the over three hundred produced had this high optical efficiency. In fact, glass placed in the etch immediately after the production of the sample plotted failed to film at all. The routine, commercial production of films of this demonstrated high efficiency would have to await the development of an extremely sensitive bath monitoring method that does not as yet exist.

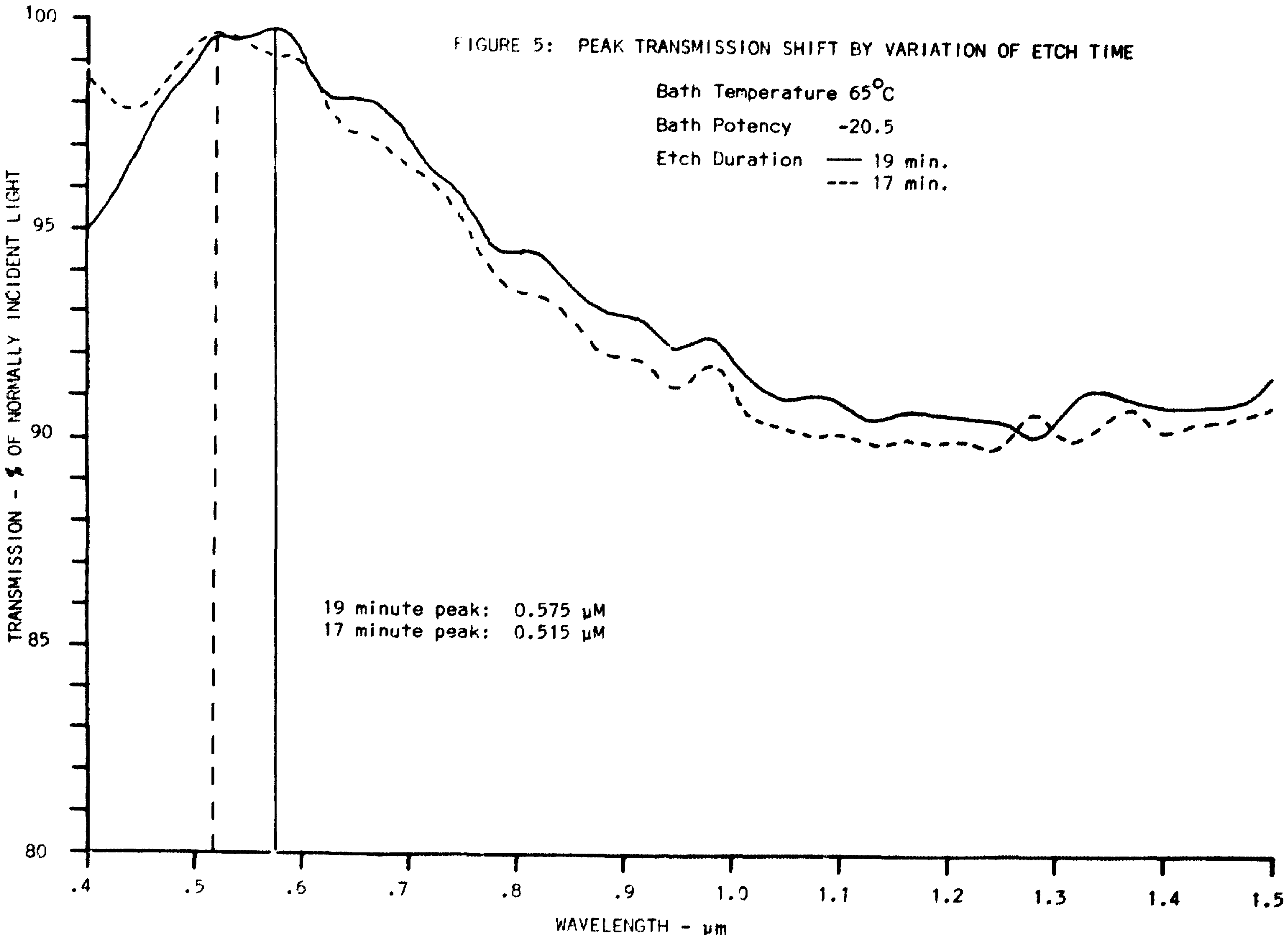


FIGURE 5: PEAK TRANSMISSION SHIFT BY VARIATION OF ETCH TIME

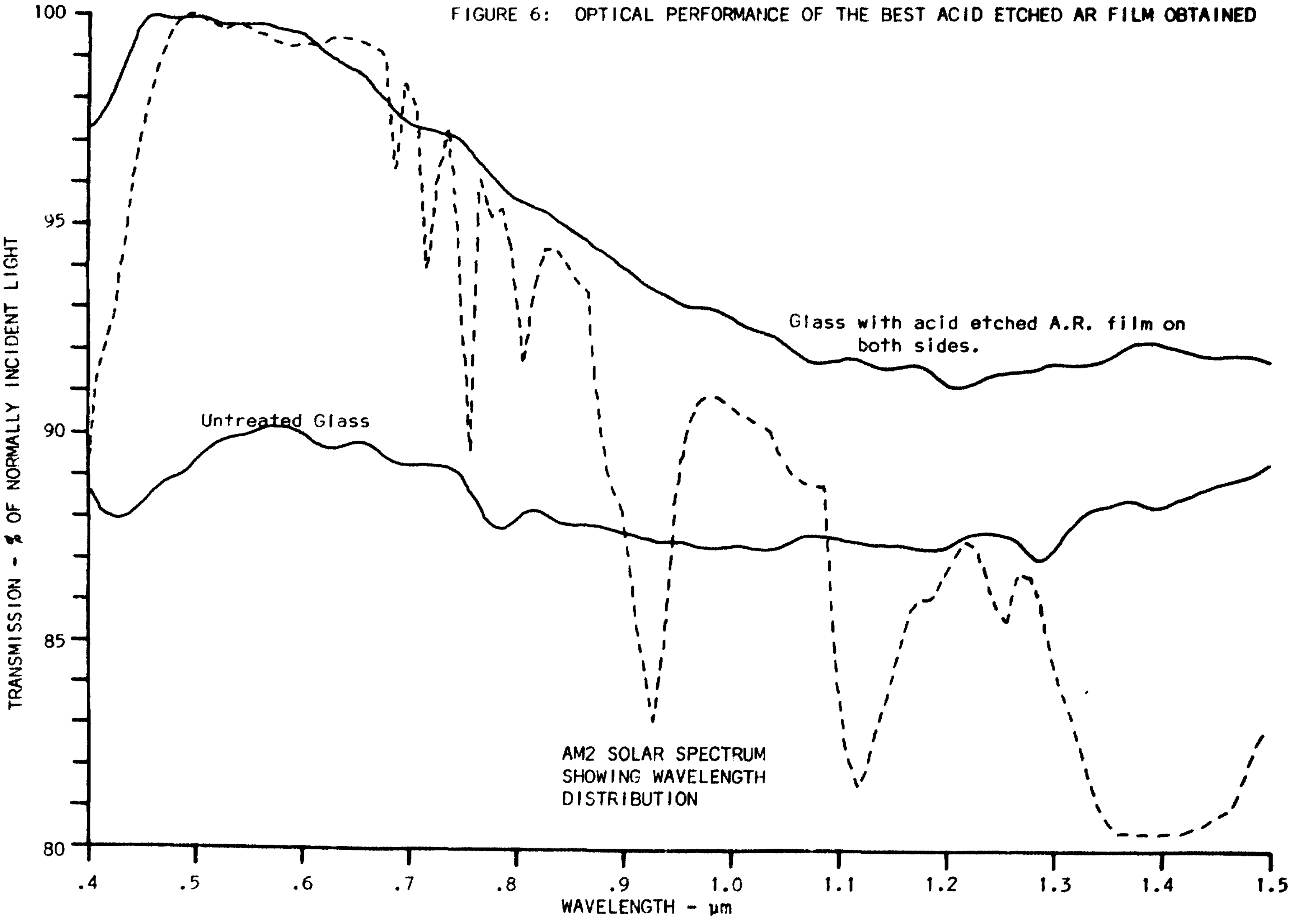


FIGURE 6: OPTICAL PERFORMANCE OF THE BEST ACID ETCHED AR FILM OBTAINED

4.0 CONCLUSIONS

1) The supersaturated silica-fluosilicic acid etch method for producing AR coatings on soda-lime glass is capable of producing coatings of excellent optical efficiency, attaining 99.8% transmission in parts of the visible spectrum.

2) The process is such that it is capable of producing AR coatings in as little as 18 minutes (65°C), and can be varied so as to shift the peak transmission wavelength of the film to any desired portion of the spectrum.

3) Stain and soil release properties are as good as those of uncoated glass. Soot release is uniformly better than plain glass. Only the removal of fingerprints presents difficulty, requiring the use of organic solvents to permit removal.

4) Chemical resistance to gaseous air pollutants is excellent. The films are susceptable to attack by commercial glass cleansers, which may not be necessary since it is demonstrated that most solid removal can be accomplished with a mild dish detergent solution.

5) The film has low abrasion resistance. From the test results and by actual experimentation, it was found that cleaning a filmed surface with a scrub brush and water will severely damage the film. Hail falling on the surface would be expected to cause damage. The use of a high pressure water spray, as from a garden hose, to clean the film also causes a reduction of AR performance. From the demonstrated physical weakness of the films we conclude that they would not maintain their excellent AR properties long enough for practical use on the external parts of solar modules. Their use on the inner, protected surfaces of concentrator and thermal panels may be advantageous, however.

6) The control of the filming solution's physical composition is difficult to perform in a way that permits large-scale production. The development of new methods of composition analysis and control, or the refinement of present methods, could change this.

7) Producing AR films by acid etching would now be prohibitively expensive because of the costs imposed by the reagents and by the expense required to support the analysis and control methods now in use. The low physical strength of the film indicates that, when used on external surfaces, it will, in all probability, not survive exposure to the environment long enough to compensate for the cost of its production.

8) Inasmuch as the filming process depends on the unique chemical composition and physical structure of soda-lime glass, the process as developed cannot be used on plastics or on borosilicate or aluminum silicate glasses.

5.0 RECOMMENDATIONS

1) The combination of low physical strength and difficult production control make current widescale use of acid etched AR films on soda lime glass impractical with today's technology and not recommended for large scale production of solar module cover glass.

2) Further research is needed to determine if acid etched films will be of benefit when used on the inner surfaces of concentrator or thermal collectors.

3) Advanced methods of analysis and control of etch solution should be investigated. Possibly the use of UV-VIS-IR spectral absorption analysis and modification of standard spectral analysis techniques may well lead to a practical control scheme.

6.0 NEW TECHNOLOGY

This project had as its purpose the investigation of an existing (albeit unused) method of producing AR films on glass. The tasks associated with the project intended to research the characteristics and potential of the process and as such were of an investigational rather than innovative nature. For this reason no new technology evolved on the contract.

7.0 COMPARISON OF METHODS

In a companion project (JPL Contract Number 955339), the production and testing of antireflective films by means of a silicate process was studied. In this section, summarized results will be used to compare the advantages and disadvantages of the methods.

7.1 PRODUCTION OF SILICATE AR FILMS

Sodium silicate is an inexpensive substance used as an adhesive, flame retardant, preservative, and filler in a number of industries. It is produced from abundant raw materials, so that a continuing supply is assured.

Sodium silicate dissolves in water to form solutions which exhibit wide variations of viscosity as a function of composition. Standard and easily performed analyses permit determination of silicate composition.

When a clean plate of glass of any type (or a sheet of certain plastics) is immersed in a dilute solution of sodium silicate and then slowly withdrawn vertically at constant speed, the silicate solution adheres to the surface of the plate and forms a liquid layer of uniform thickness. Upon brief exposure to air, the layer dries to a film of solid sodium silicate. Subsequent exposure to sulfuric acid converts the film to sodium sulfate and silicon dioxide, in either anhydrous or low-hydrated form. The silica-sulfate layer is quite insoluble and the plate and film can then be rinsed with water and dried. By proper choice of sodium silicate solution concentration and the speed at which the plate is withdrawn, the thickness of the final silica-sulfate film can be controlled to the extent that it can be made thin enough to function as an antireflective film. Even though technically a misnomer, films of this type will be referred to as silicate films.

7.2 COMPARISONS

Below are presented, in outline form, comparisons of chemical, physical, and soil resistance, was well as notes on process control.

7.2.1 OPTICAL PERFORMANCE

Figure 7 illustrates the light transmission characteristics of a silicate film in comparison with the best obtained acid etched film and untreated glass. A plot of the AM2 solar spectrum is drawn to arbitrary scale to permit comparison of transmission peaks with peaks in the solar spectrum. Silicate films characteristically display a poorer antireflective effect than acid etched films. The superiority of silicate films lies in their ease of production and physical strength.

7.2.2 PROCESSING COMPARISON

Acid Etching

1. Process is difficult to control
2. Processing equipment is relatively inexpensive and simple
3. Process requires relatively expensive reagents and preparation.

Silicate

1. Process is easily controlled
2. Processing equipment is more expensive than that required for acid etching, but is available.
3. Production is less expensive than for acid etching.

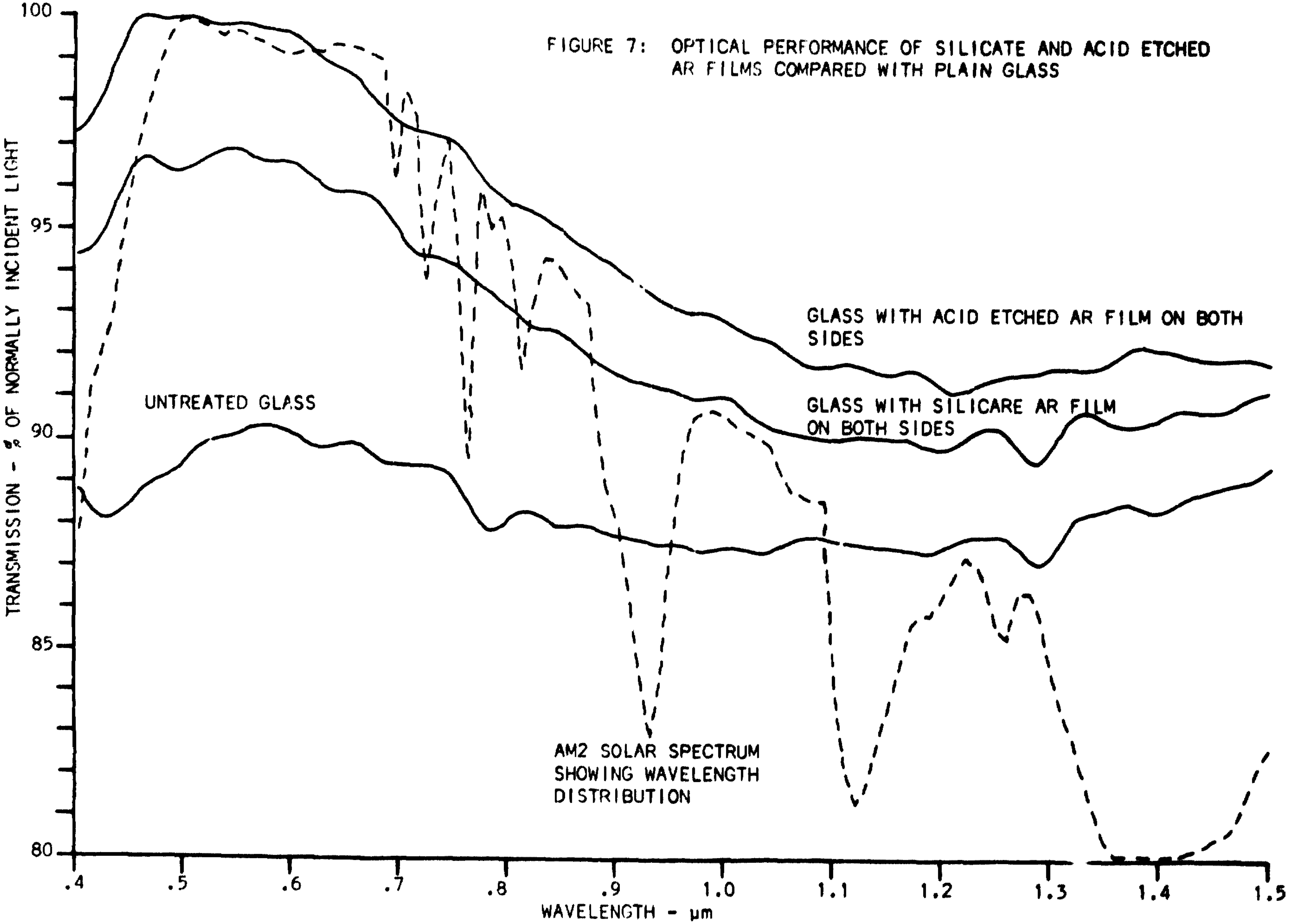


FIGURE 7: OPTICAL PERFORMANCE OF SILICATE AND ACID ETCHED AR FILMS COMPARED WITH PLAIN GLASS

7.2.3 STAIN RESISTANCE

The stain resistance of silicate films is identical to that of acid etched films and to untreated glass.

- Saturated dye solutions applied to glass
- Baked at 60°C for 2 hours
- Removal attempted by:
  - water rinse
  - water soak and light wiping
  - alcohol soak and wiping
- Results were the same for both types of film and for glass

STAIN	RESULT
Brilliant Green	Rinsed off with water
Crystal Violet	Rinsed off with water
Cresol Red	Rinsed off with water
Aniline Blue	Rinsed off with water
Sodium Fluorescein	Rinsed off with water
India Ink	Wiped off with water
Sudan IV	Wiped off with alcohol

7.2.4 SOIL RESISTANCE

- Results were the same for both types of film and for glass
- Soils were applied and baked at 60°C for 2 hours.

SOIL	RESULT
Peanut Butter	All removed by detergent wipe
Corn Syrup	
Mucilage	
Egg	
Evaporated Milk	
Shoe Polish	Removed by methylene chloride

Fingerprints were less noticeable on, and more easily removed from, silicate filmed glass.

7.2.5 CHEMICAL RESISTANCE

The resistance of silicate films to chemical attack is essentially the same. Both types of film are attacked by high pH glass cleaners, and both suffered some loss of transmission in the short wavelength area of the visible spectrum after being exposed to a prolonged water blast.

7.2.6 ABRASION RESISTANCE

Figure 8 shows the results of abrasion testing on silicate films, as well as on the acid etched films reviewed in this report. Silicate films are clearly superior in abrasion resistance.

7.2.7 SUMMARY

	ACID ETCH PROCESS	SILICATE PROCESS
Process Control	Very Poor	Very Good
Optical Efficiency	Good - Excellent	Fair

Stain Resistance	Excellent	Excellent
Soil Resistance	Excellent	Excellent
Chemical Resistance	Fair	Fair
Abrasion Resistance	Very Poor	Good

FIGURE 8

ABRASION TEST RESULTS

ABRASION PAD: 4 layers 0.02 cm (0.008 inch) cotton duck, 13.9 cm^2 area

PRESSURE: 138 g/cm^2

ABRASIVE: Buehler No. 40-6475 AB, 3200 mesh

STROKES REQUIRED

TEST FILMS

⟶ INCREASING TRANSMISSION

ABRASIVE	EFFECT	SILICATE	ACID ETCHED #1	ACID ETCHED #2	ACID ETCHED #3
CLOTH ONLY	FIRST SIGN OF DAMAGE	>200	80	30	20
	MODERATE DAMAGE	---	200	100	50
CLOTH PLUS ABRASIVE	FIRST SIGN OF DAMAGE	100	20	1	1
	MODERATE WEAR	300	200	40	20
	FILM REMOVED	>500	>300	200	150

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