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ANTI-REFLECTION COATINGS

ON

LARGE AREA GLASS SHEETS

FINAL REPORT
MOTOROLA REPORT NO. 2366/4
DRD NO. SE-5

SEPTEMBER 1980

JPL CONTRACT NO. 955339

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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

Antireflective coatings which may be suitable for use on the covers of photovoltaic solar modules can be easily produced by a dipping process. The coatings are applied to glass by drawing sheets of glass vertically out of dilute aqueous sodium silicate solutions at a constant speed, allowing the adherent liquid film to dry, then exposing the dried film to concentrated sulfuric acid, followed by a water rinse and dry.

The process produces coatings of good optical performance (96.7% peak transmission at 0.540 μM wavelength) combined with excellent stain and soil resistance, and good resistance to abrasion. The process is reproducible and easily controlled.

TABLE OF CONTENTS

<u>SECTION NUMBER</u>	<u>TITLE</u>	<u>PAGE</u>
1.0	Summary	1
2.0	Introduction	2
3.0	Technical Discussion	7
3.1	The Silicate Process	7
3.2	Experimental Procedure	9
3.2.1	Choice of Glass	9
3.2.2	Preparation of Glass	9
3.2.3	Preliminary Considerations	10
3.2.3.1	Dust Control	12
3.2.3.2	Carbon Dioxide	13
3.2.3.3	Humidity Effects	14
3.2.3.4	Filming Apparatus Configuration	15
3.2.4	Silicate Solution Preparation and Effects	16
3.2.4.1	Choice of Silicate	16
3.2.5	Withdrawal Speed Effects	20
3.2.6	Potential of the Process	23
3.3	Durability Testing	25
3.3.1	Physical Abrasion	25
3.3.2	Chemical Resistance	26
3.3.2.1	Fume Exposure	26
3.3.2.2	Cleaning Agents	27
3.3.2.3	Water Blast and Boil	29
3.3.3	Stain and Soil Resistance	30
3.3.3.1	Stains	32

<u>SECTION NUMBER</u>	<u>TITLE</u>	<u>PAGE</u>
3.3.3.2	Soils	33
3.3.3.3	Soot	34
3.3.3.4	Fingerprints	34
4.0	Conclusions	35
5.0	Recommendations	37
6.0	New Technology	38
7.0	Comparison of Methods	39
7.1	Production of Acid Etched AR Films	39
7.2	Comparisons	40
7.2.1	Optical Performance	40
7.2.2	Processing Comparison	40
7.2.3	Stain Resistance	42
7.2.4	Soil Resistance	42
7.2.5	Chemical Resistance	43
7.2.6	Abrasion Resistance	43
7.2.7	Summary	43
8.0	References	46

LIST OF FIGURES

<u>FIGURE NUMBER</u>	<u>TITLE</u>	<u>PAGE</u>
1	Theory of Antireflective Films	5
2	Effect of Silicate Concentration	19
3	Effect of Withdrawal Speed on Optical Performance	21
4	Simultaneous Variation of Speed and Silicate Concentration	22
5	Silicate AR Film Performance	24
6	Effect of Running Water on Optical Performance of Silicate AR Film.	28
7	Effect of Removal of Water Soluble AR Film Components	31
8	Comparative AR Coating Performance	41
9	Abrasion Test Results	45

LIST OF TABLES

<u>TABLE NUMBER</u>	<u>TITLE</u>	<u>PAGE</u>
1	Physical Properties of Silicate Solutions	18

1.0 SUMMARY

The increasing level of manufacture of solar modules with their large glass cover plates has revived interest in low cost AR films 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. A potentially useful process for this purpose involves the formation of a film of sodium silicate on the surface of a cover sheet by dipping. The silicate film is then exposed to sulfuric acid to render it hard and insoluble, then rinsed and dried.

The optical efficiency of such a film is good, peak transmission of 96.7% being obtained at 0.54 μm as opposed to a peak transmission of 90.1% (at 0.570 μm) for untreated glass.

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

The film is very durable, resisting mechanical abrasion well and displaying outstanding resistance to soiling and staining. In addition the production process for producing film is practical, controllable, and reproducible.

The silicate process appears feasible for immediate use, and will become additionally attractive if (as appears possible) optical performance of the AR film can be improved, and after long term stability has been verified by extended weather exposure studies.

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, atmospheric constituents, 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

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

where

R = fraction of light reflected

n_o = refractive index of air ≈ 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 of 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 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 at the bottom glass surface. Although organic encapsulants are 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.

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

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

where

n_f = refractive index of the film

n_c = refractive index of the cover material

d_f = thickness of the film

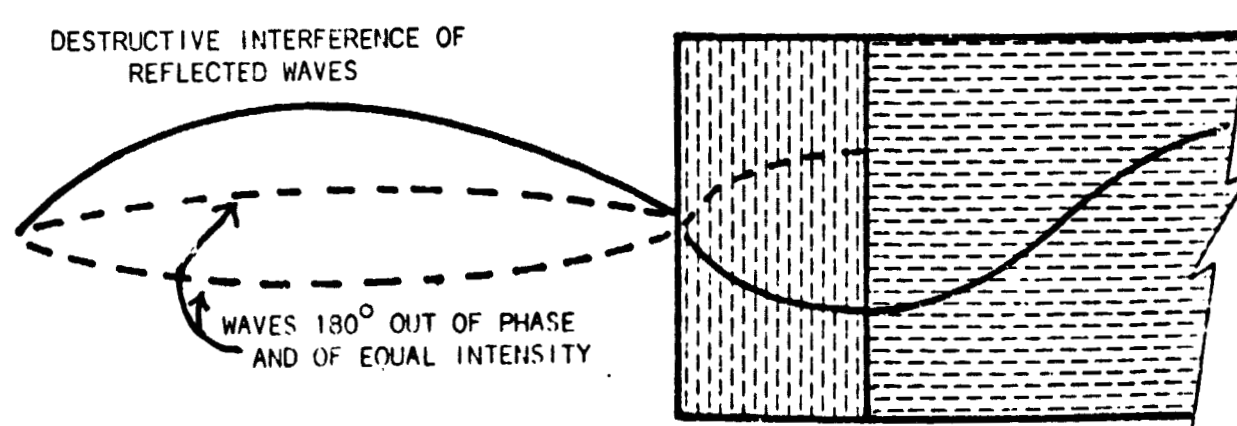
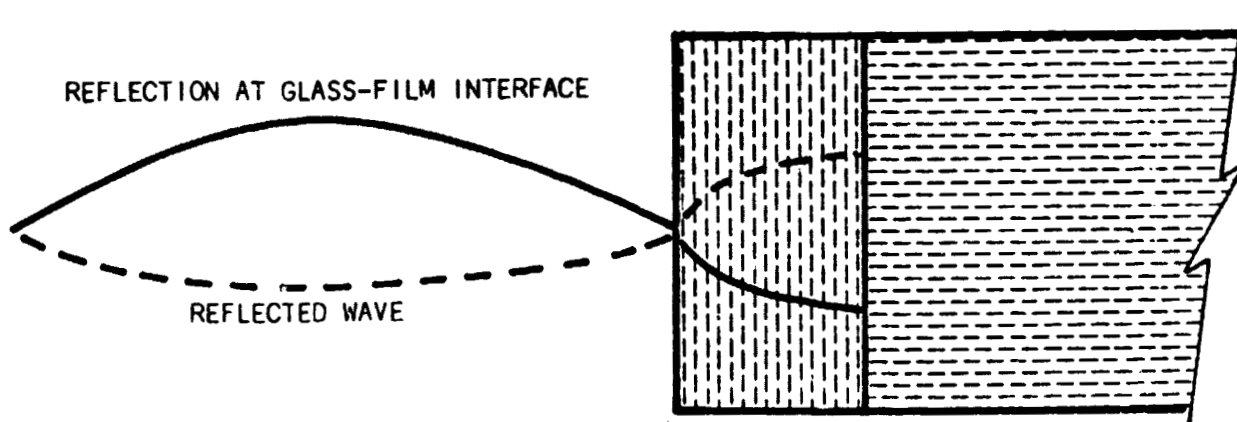
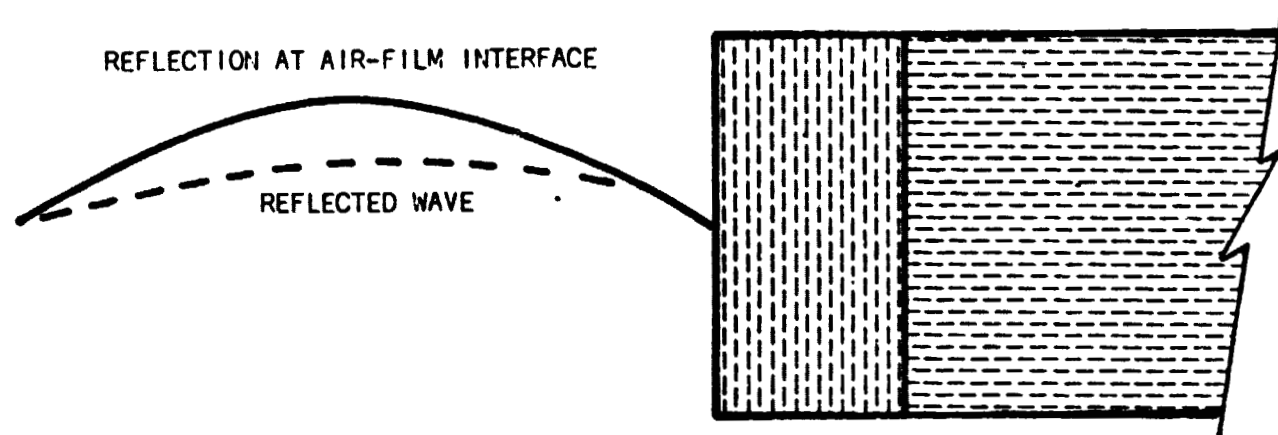
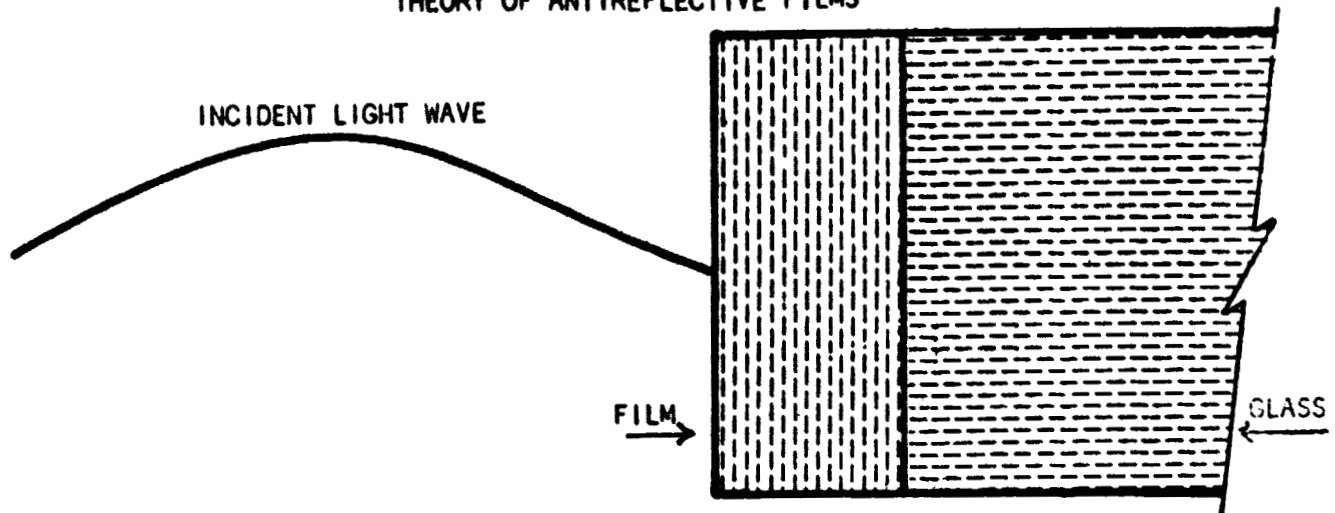
λ = wavelength of incident light.

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 indices permitting 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 $\sqrt{n_{\text{glass}}}$. The wave reflected at the

THEORY OF ANTIREFLECTIVE FILMS



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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 $\frac{1}{2}\lambda$ 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.

3.0 TECHNICAL DISCUSSION

3.1 THE SILICATE PROCESS

One way of producing antireflective films on glass or other substances without recourse to evaporation is by applying a liquid that can be dried or otherwise hardened to form a very thin, tough layer suitable for use as an AR coating.

Alkali silicates comprise one group of substances suitable for the production of AR coatings. The silicates are water soluble, so that they can be diluted to any desired concentration. They are inexpensive, being manufactured from sand or some other abundant form of silica and other compounds such as sodium carbonate derived from common salt. The silicates are also readily available -- especially sodium silicate -- which is used in industry as an adhesive, binder, flame retardant, preservative, and filler.

When exposed to certain other compounds, notably mineral acids, sodium silicate gels, forming silica -- usually in hydrated form -- and a sodium salt, the exact composition of which depends on the acid used. The hydrated nature of silica gel can be varied by the choice and concentration of the acid and silicate used so that tough, durable, low hydrated gels can be produced which are suitable for optical use.

In the past, the utility of silicate solutions for the production of AR coatings was recognized. One of the earliest modern references described the production of decorative iridescent films on glass. (1) Later work, about the time of World War II, was directed at the production of AR coatings on optical components. At the time, the methods of coating production by vacuum evaporation that are in use today had not been perfected and were regarded as being cumbersome

and unreliable. Some of the efforts yielded desirable results. Vail (2) gives a brief but informative account of some successful techniques that were developed.

The methods developed for optical purposes were generally complex, involving the use of acidified silicate solutions (which could not be stored) and various wetting agents. In some instances, centrifugation was also used in order to thin and level the silicate solutions on the surfaces to be coated. These complications argue against the use of the same techniques for large area module covers. Some other methods employ the deposition of an already gelled dispersion of silica and baking of the deposit to harden it, a method that may be practical but is still inconvenient.

A new method of producing silicate coatings on surfaces has been developed which uses simply prepared silicate solutions and which does not require centrifugation or similar inconvenient processing operations.

The process begins with sodium silicate in its common commercial form, i.e. already dissolved in water to form a thick syrup. The syrup is first diluted with water to form a thin liquid. Solutions approximating 10 volume percent of sodium silicate syrup were found to be convenient. Clean dry sheets of glass are then dipped into the solution and withdrawn at constant speed, producing a thin, even coating of sodium silicate solution on the surface of the glass. After withdrawal, the glass with its adherent coating of silicate is allowed to dry. Next, the glass is dipped into sulfuric acid to convert the dry silicate film into a silica-sodium sulfate film. Concentrated sulfuric acid is preferred over dilute acid because the concentrated acid yields silica in either anhydrous or low-hydrated form, which is more durable than the gelatinous highly hydrated forms of silica. After the sulfuric acid dip, which typically lasts for one or two minutes, the glass is rinsed in water and

dried. The process is then complete. The term "silicate film" will be used to identify the finished, acid hardened coating, even though this is technically a misnomer since the coating consists not of silicate but of silica and sodium sulfate.

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 and the stability of the silicate solution 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 silicate solution.

3.2.3 PRELIMINARY CONSIDERATIONS

When a wettable surface is submerged below the surface of a quiescent liquid and then withdrawn vertically at constant speed, a film of liquid adheres to the surface. The thickness of the adherent liquid film is constant and predictable; its thickness is a function of several fluid properties and the speed of withdrawal. A mathematical analysis has been developed and yields the following equation (4):

$$h_o = 0.93 \frac{(\mu v)^{2/3}}{\sigma^{1/6} (\rho g)^{1/2}} \quad (4)$$

where h_o = film thickness
 μ = viscosity
 v = withdrawal speed
 σ = surface tension
 ρ = density
 g = acceleration of gravity

Examination of Equation 4 shows that speed of withdrawal and liquid viscosity contribute most significantly to the determination of film thickness,

while liquid density is of secondary importance and liquid surface tension is the least consequential. Since part of the intention of this project was to identify a successful filming process, this set of circumstances was fortunate. In the course of our experiments, the speed of withdrawal of glass plates from the solution was varied. In addition, the viscosity and density of the silicate solutions from which the glass was withdrawn were varied by diluting the solutions with water. In this way, the three most significant determinants of film thickness were varied over wide ranges. Surface tension -- the least significant property in determining film thickness -- is the property most difficult to control and measure. (It was measured in the experiments but no attempt at control was made.) Surface tension was found to be comparable to that of water and was unvarying over the range of silicate concentrations found to produce desirable films, as was to be expected of aqueous solutions of simple salts. Attempts at control of surface tension would have required recourse to soap or detergent additives to the silicate filming solutions, thus complicating the process and, in some cases, causing precipitation or gelling of the sodium silicate.

The procedure necessary to produce effective AR films was determined empirically. Although, as cited earlier, an analytic method for prediction of liquid film thickness exists, it was used for guidance only since drying of the liquid film and its exposure to sulfuric acid varied the ultimate thickness of the film obtained at the end of the process.

During early experiments some practical matters of technique were found to be very important to the success of the process and influenced the design of the final experimental apparatus. These matters will be discussed now, before a description of the actual experimental variations.

3.2.3.1 DUST CONTROL

At the beginning of this program, it was assumed that the atmosphere present during film formation would have some effect on the quality of the film produced. This has been shown to be the case, and the most obvious problem is that of dust. Ordinary lint and airborne dust are extremely troublesome when films are formed in ordinary air. The dust particles attach themselves to the wet surface of freshly drawn films and cause, by capillary action, bulging of the film around the particles. This is noticed as scattered points of off-color film after the silicate solution has dried. Depending on the nature of the dust, darkening of the film may occur when the film is exposed to sulfuric acid. Lint, hair, and other particles of biological origin are particularly susceptible to charring during the sulfuric acid soak, thus darkening the film. Gritty dusts of presumed mineral or industrial origin are generally opaque to begin with; while they do not darken on exposure to sulfuric acid, they still produce variations in film thickness and cause diminished light transmission because of their opacity. Films prepared in a filtered, laminar-flow airstream were found to be of better quality than those formed in ordinary room air, but some dust particles still appeared on the wet film. Early attempts at filtration employed spongy plastic filters similar to those used in room air conditioners; later cloth and paper filters of finer mesh were tried. All of these filters proved unsatisfactory, the plastic sponge filter was far too porous to catch all but the largest dust particles, while the cloth and paper filters merely replaced the dust originally in the air with fibers from themselves. At this point it was decided to test one of the gas filters available commercially. A non-shedding cartridge filter - Pall 0.35 micron Ultipore DFA-UFA Disposable Filter Assembly - was tested and found satisfactory at removing all detectable dust from the gas surrounding the filming glass.

3.2.3.2 CARBON DIOXIDE

After a silicate film is formed and dried, it is normally dipped in sulfuric acid promptly in order to harden the film and convert it to insoluble components. If the sulfuric acid dip is delayed, carbon dioxide in the atmosphere reacts with the film.

It is known that alkali silicates absorb gaseous carbon dioxide, reacting to form alkali carbonates and hydrated silica. The reaction of a film with atmospheric carbon dioxide results in clouding of the film with consequent loss of transparency. Treatment with sulfuric acid offers no improvement -- the alkali carbonates formed in the silicate film effervesce on contact with sulfuric acid, causing disruption of the film.

At the carbon dioxide concentrations commonly found in the atmosphere, noticeable film clouding requires about 24 hours to occur. If, for some reason, the sulfuric acid dip of silicate filmed glass must be delayed for more than a day, storage of the filmed glass in an inert atmosphere is necessary.

In addition to clouding of silicate films by CO_2 , a similar but much slower clouding of the silicate solution from which the film is drawn occurs. Clouding of silicate solutions becomes noticeable after about a week in 2 liter silicate batches with a surface area of 120 cm^2 . Again, clouding of the solution indicates an undesirable change in chemical composition.

In view of the fact that silicate solutions are unstable, over long periods of time, in an atmosphere of carbon dioxide, it was decided to enclose the filming apparatus in a nitrogen atmosphere. The N_2 atmosphere permitted use of solutions for longer than five weeks without noticeable degradation, and silicate coated glass suffered no damage even when sulfuric acid treatment was delayed for a week after filming.

3.2.3.3 HUMIDITY EFFECTS

It was originally thought that the introduction of nitrogen of a controlled humidity to the chamber in which filming is conducted would promote the formation of unusually smooth films (by delaying drying long enough to allow the fluid to level itself on the glass) or allow fine control of film thickness (again by delaying drying long enough to allow additional draining of filming fluid from the glass surface). In contrast to the expected results, humidification resulted in uneven films and increased dust contamination of films.

Experiments were conducted by bubbling nitrogen through water at various temperatures before admitting the N_2 into the filming chamber. At all levels of humidification the moist nitrogen delayed drying of the film drastically -- long enough for the wet film to catch the few dust particles that enter the chamber from the outside when glass is inserted into the chamber, and also long enough for air currents to disturb the liquid film and cause it to become uneven. Additionally, the drying process itself took much longer than was convenient for efficient production. The hygroscopic nature of sodium silicate contributed to the problem by selectively absorbing moisture from the atmosphere and multiplying the effect of even slight humidity.

In view of the results of these experiments, it was found that dry N_2 provided the atmosphere most conducive to reproducible film formation. In the system, granular potassium hydroxide was employed as a dessicant, and was placed in an open vessel directly in the chamber rather than in the incoming N_2 line. This arrangement permitted the dessicant to remove moisture generated by evaporation from the filmed sheets and the filming solution reservoir itself, and admitted by opening the chamber to insert glass samples.

3.2.3.4 FILMING APPARATUS CONFIGURATION

The observations presented in Sections 3.2.3.1 through 3.2.3.3 were used in constructing a device for the production of filmed glass samples for optical and physical testing.

A plexiglas chamber 30 centimeters on a side was constructed to serve as protection against dust and atmospheric humidity and CO_2 . The cube was provided with a 20 cm square access door in one side through which glass samples could be inserted and withdrawn. In one corner of the cube a gas port admitted dry nitrogen which had been filtered through a Pall 0.35 micron Unipore DFA-UFA Disposable Filter Assembly. Nitrogen flow rate into the chamber was approximately 5 L/minute. In the center of the chamber was placed a quartz vessel which was filled with the silicate solution under study. Through a small hole in the top of the vessel a nylon cord with a clamp on the end was suspended over the silicate container. The cord was attached to a variable speed drive outside the vessel. Glass sheets attached to the clamp were lowered and raised in and out of the silicate solution by means of motion transmitted along the cord. Also provided inside the chamber was a small beaker of potassium hydroxide pellets; this served as an additional dessicant to remove moisture generated by evaporation of the silicate solution.

In operation, a silicate solution of a particular concentration was placed in the quartz vessel. In the clamp above the solution was mounted a glass plate, which was lowered into the solution and then withdrawn by means of the constant speed drive. After withdrawal, the glass plate was suspended above the silicate vessel for two minutes to allow the liquid silicate film to dry. The plate was then removed, submerged in 96% sulfuric acid for two minutes, and rinsed in flowing deionized water for five minutes. After the water rinse, the

plate was flushed with isopropyl alcohol and dried by exposure to hot freon fumes in a vapor degreaser. This drying technique eliminated the abrasive effects that manual drying with cloth may have had and presented the plates with a clean dry surface unaltered by physical handling. A number of plates were produced from each specific silicate solution by varying the speed of withdrawal from the solution.

3.2.4 SILICATE SOLUTION PREPARATION AND EFFECTS

3.2.4.1 CHOICE OF SILICATE

The sodium silicate chosen for the investigation was Humco Sodium Silicate which is readily available and can even be purchased in pharmacies. The silicate syrup is intended for use as a food preservative or adhesive, and represents an inexpensive grade of silicate which has not undergone any special manufacturing processes. It was our intention to verify the success of the silicate AR process even with this grade of material -- a "worst case" situation. The silicate syrup as received had the following characteristics:

Density	1.5 G/cm ⁴
pH	11.3
Dry Residue	54.1 wt. %
Na Content	5.0 wt. %
Si Content	12.0 wt. %
Na ₂ O/SiO ₂	0.26

The sodium silicate syrup itself is of much too high a viscosity to be used in coating glass without being diluted. Solutions of the syrup in deionized water were prepared. At the start of our investigations, solutions ranging from

one to fifty volume percent of sodium silicate syrup in water were studied. Of these, those ranging from 5 to 16 volume percent were found to produce films of some AR effectiveness at withdrawal rates of from 0.13 to 0.54 cm/second. The concentrations, densities, viscosities, and surface tensions of the successful solutions are listed in Table 1.

Solution densities were measured by use of a pycnometer, viscosities were determined using an Ostwalt capillary viscometer, and surface tension was measured by means of the capillary rise technique using soda-lime glass tubes. All measurements were performed at an ambient temperature of 21°C.

The effects of solution viscosity and density were surprisingly large. At silicate concentrations above 14 volume percent, all attempts at drawing film -- at any speed -- resulted in the formation of a film of uneven thickness, as evidenced by the appearance of swirls of color similar to those seen in soap bubbles. In extreme cases, the films were thick enough to display no color whatsoever. These films generally crazed when dried and exposed to the sulfuric acid dip. At silicate concentrations below nine volume percent, the films formed, although even in color, were ineffective in significantly increasing light transmission.

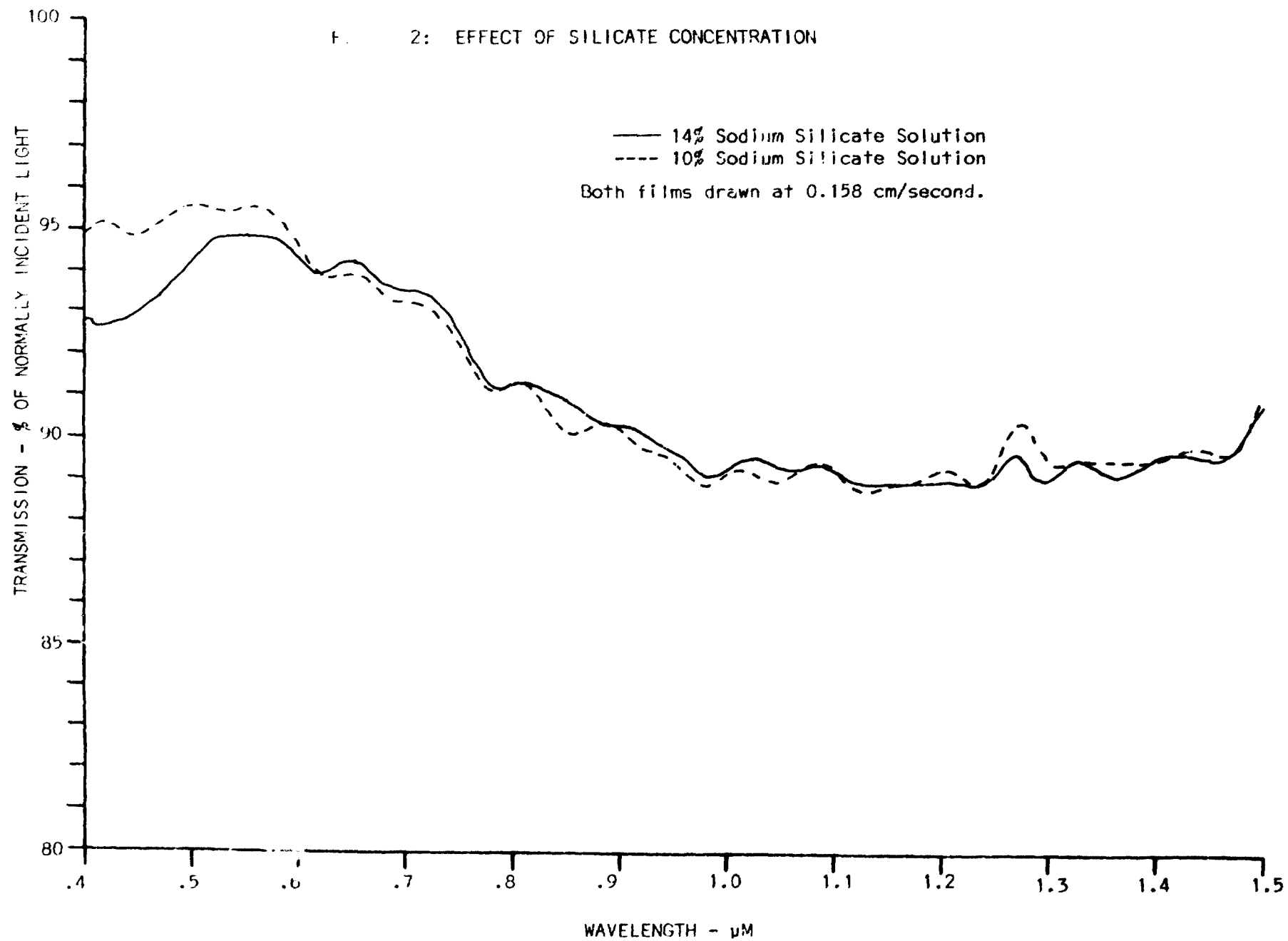
Silicate concentrations between nine and fourteen volume percent produced films that appeared to have the most pronounced effect as judged by the unaided eye. In these cases, the films displayed a deep, even color, caused by the preferential (but reduced) reflection of visible light.

The primary effects of concentration variations were to subtly alter the amount of light transmitted and to increase the wavelength of most-transmitted light.

Figure 2 shows transmission plots of plates filmed with ten and fourteen percent solutions withdrawn at the same speed -- 0.158 cm/second. Even though

TABLE 1
PHYSICAL PROPERTIES OF SILICATE SOLUTIONS

SILICATE SOLUTION	VOLUME % SILICATE SYRUP	DENSITY G/mL	VISCOSITY CENTIPOISE	SURFACE TENSION DYNES/CM
5	5	1.0205	1.0222	74
7	7	1.0402	1.0534	74
9	9	1.0495	1.0850	74
10	10	1.0531	1.1073	74
12	12	1.0585	1.1590	74
14	14	1.0605	1.2377	74



a concentration change from 10 to 14 percent is relatively large, the only effect is a slight decrease in transmission in the short wavelength region of the visible spectrum.

On the basis of data collected, the most effective AR films are obtained with solutions of 9 - 10 volume % silicate concentration.

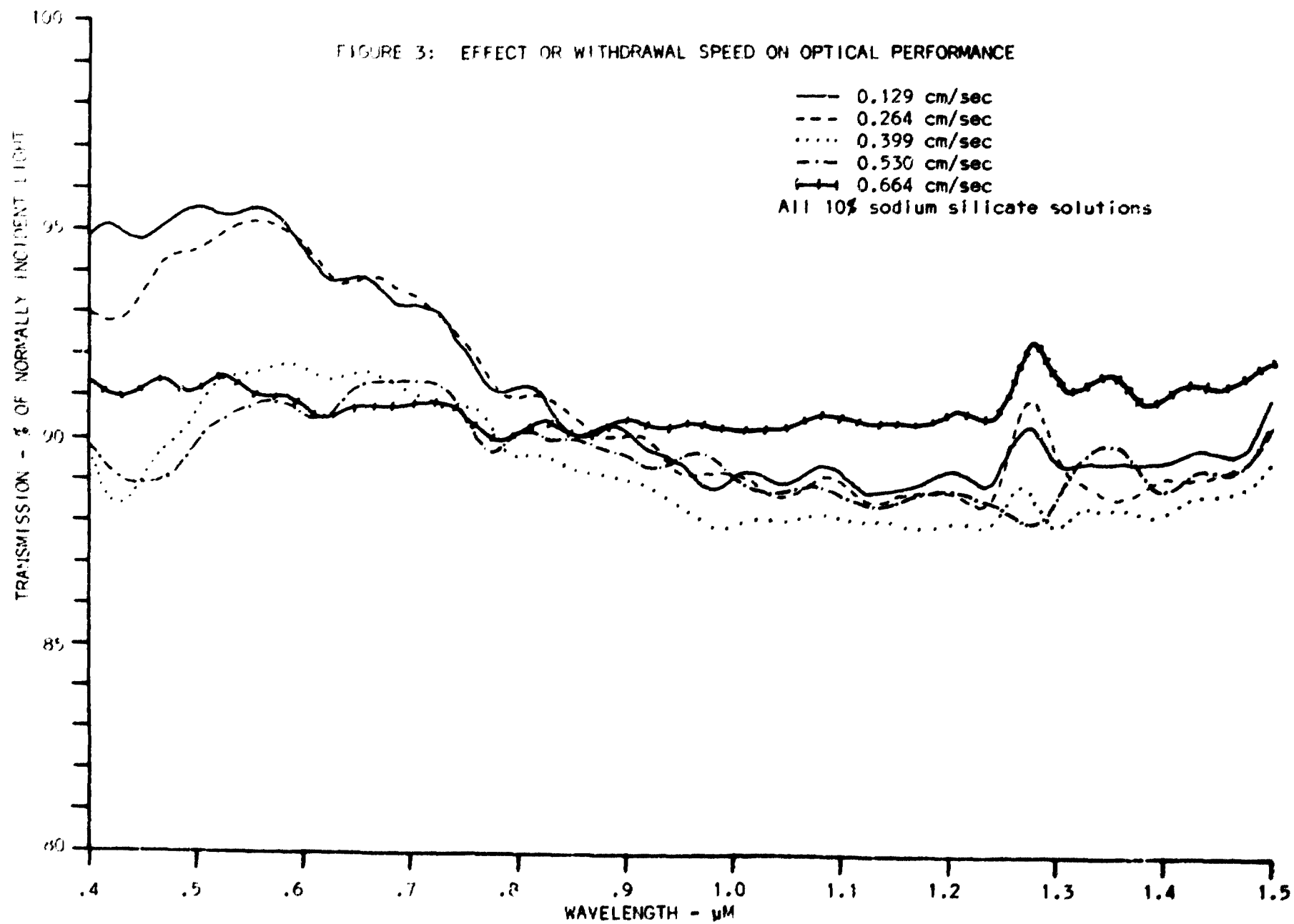
3.2.5 WITHDRAWAL SPEED EFFECTS

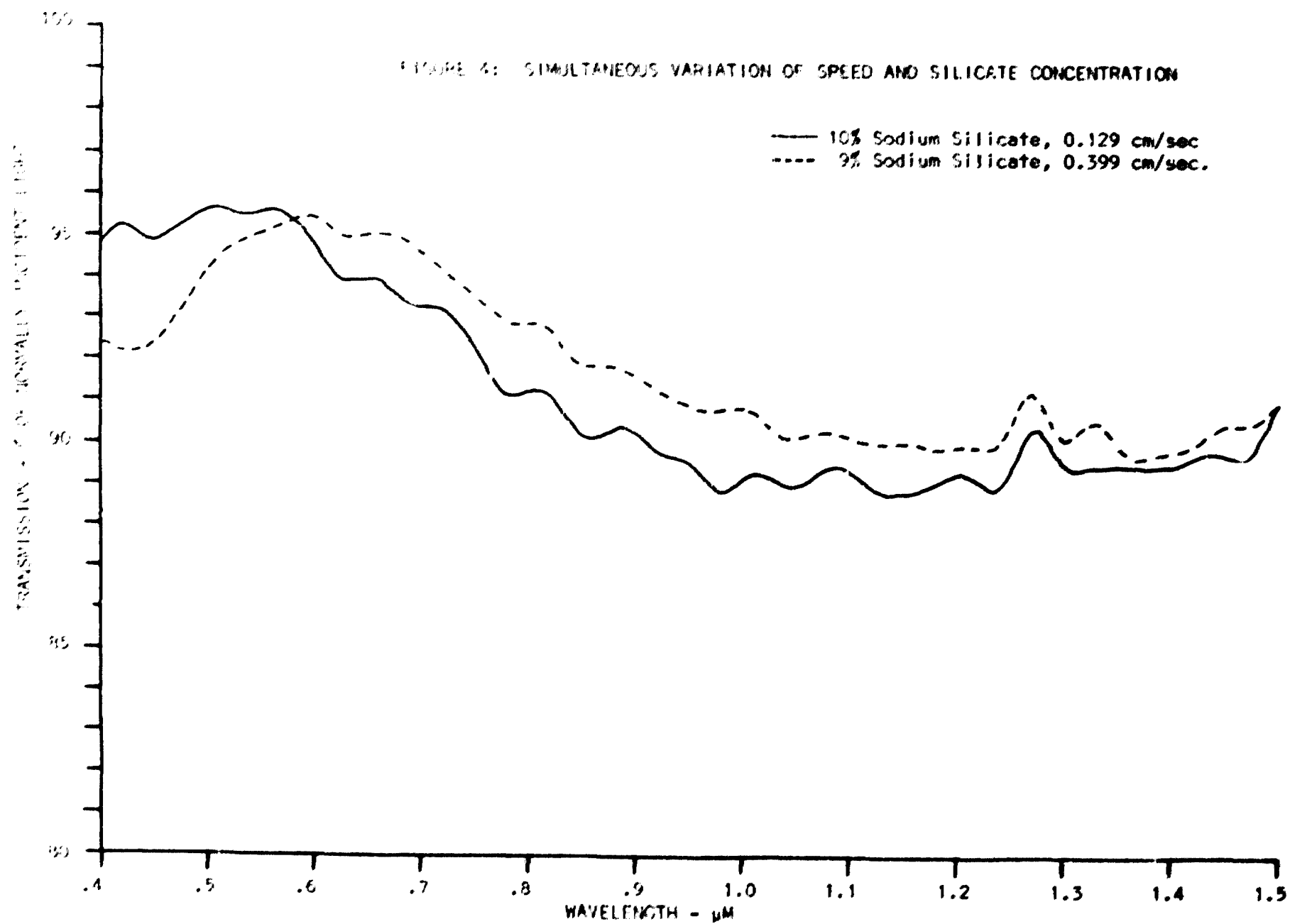
As mentioned earlier in Section 3.2.4.1 withdrawal speeds ranged from 0.13 to 0.54 cm/second. This range encompassed the effective speeds for all of the silicate solutions tested.

As with variations in silicate concentration, variation of withdrawal speed altered both the wavelength of peak transmission and the overall effectiveness of the AR coating produced. Figure 3 illustrates the effects of variations of speed on transmission performance of glass plates coated with a 10 volume percent silicate solution. On the basis of AR effectiveness, a withdrawal rate of 0.35 cm/sec appears optimum. Since the use of a higher speed of withdrawal can be expected to increase the thickness of a film (as shown by Equation 4), it was felt that the use of a more dilute silicate solution (which would decrease film thickness) might be used with higher withdrawal speed -- the opposite effects of these variations were expected to cancel each other. The higher withdrawal rate offers the advantage of faster processing.

Figure 4 shows the transmission performance of films drawn from a 10% solution at low speed and a 9% solution at high speed. The effects of speed and concentration do not precisely cancel each other; while the percentage of peak transmission remains the same, an obvious shift toward transmission of longer wavelengths results in the high-speed, dilute film. The demands of limited

FIGURE 3: EFFECT OF WITHDRAWAL SPEED ON OPTICAL PERFORMANCE





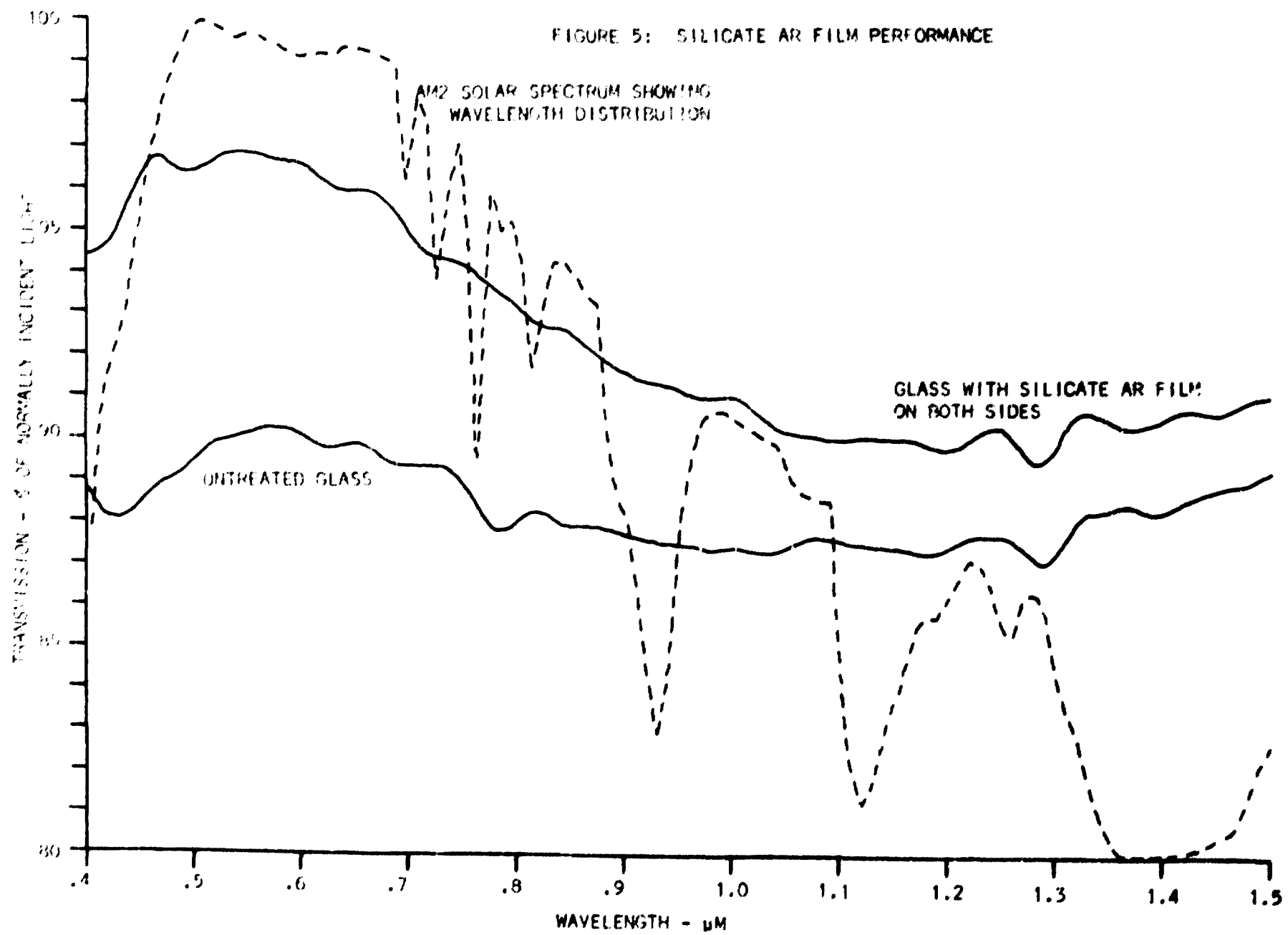
time prevented exhaustive investigation of the possibility of exactly compensating for fast withdrawal rates with more dilute silicate solutions and avoiding or controlling the wavelength shift shown, but it can be concluded that the AR properties of a silicate coating can be controlled easily, and to a great extent, by altering withdrawal speed and silicate concentration.

On the basis of optical measurements of AR performance, the most effective AR films are produced by use of 9% silicate solutions at 0.4 cm/second or by 10% silicate solutions at withdrawal speeds of 0.13 cm/second. In either case, the withdrawal speeds are not prohibitively slow. Even at the lower speed of 0.13 cm/sec. and, 4 foot square sheets of glass can be coated with silicate in less than 16 minutes. The use of clamps allowing the dipping of multiple sheets of glass at one time permit significant reduction of the amount of time required to film a given area of glass.

3.2.6 POTENTIAL OF THE PROCESS

It was noted earlier that the method of coating chosen was a very simple one, and that the choice of silicate used represented a "worst case" approach to filming, since silicate purity and clarity are not of concern in a substance intended for use as a household adhesive. With some refinements of technique, such as filtration of the silicate solution, and the use of freshly prepared solution, AR results even better than those illustrated in the previous sections can be obtained. Figure 5 shows transmission characteristics of the best silicate film obtained. Also shown are the transmission curves for uncoated glass, and a representation of the air mass 2 solar spectrum.

The AR effectiveness of silicate films may be enhanced by weathering; discussion of this effect is presented in Section 3.3.2.3.



3.3 DURABILITY TESTING

3.3.1 PHYSICAL ABRASION

The durability of an AR 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 effective 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.

In order to test abrasion resistance, five samples of filmed glass were prepared by withdrawal from 10 volume percent silicate solution at 0.094 cm/second. The samples were treated with sulfuric acid, then rinsed and dried as detailed in Section 3.2.3.4. All samples were uniform in film color and were free from defects.

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 0.008 inch cotton duck, with a circular area of 1.39 cm^2 . The pad was loaded with weights to yield a pressure of 138 g/cm^2 . After conducting abrasion tests with the pad alone on five 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. Testing was performed by moving the pad laterally across the filmed glass surface in 2 inch strokes, with visual inspection of the glass after every 5 strokes. Below is summarized the result of the tests.

ABRASIVE	EFFECT	STROKES REQUIRED
Cloth	First sign of damage	> 200
	Moderate Wear	---
Cloth Plus Abrasive Powder	First sign of damage	100
	Moderate Wear	300
	Film Removed	> 500

As shown above, films produced by the silicate process are especially rugged. With cloth alone, over 200 strokes were required to cause any sign of damage to the film. The "over" designation was used because of the ambiguous appearance of damaged film. No easily identified scratches or other marks appeared, but rather, there occurred a gradual change in film color that was difficult to detect visually. Moderate wear was defined as unmistakable damage covering the entire stroked area but not resulting in complete removal of film from any area. Without abrasive, it was impossible to produce this kind of damage.

With the abrasive, endurance of the films was still remarkable. Complete removal of film was not accomplished, the 500 strokes listed represents removal of 95% of the film in the stroked area.

3.3.2 CHEMICAL RESISTANCE

3.3.2.1 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.

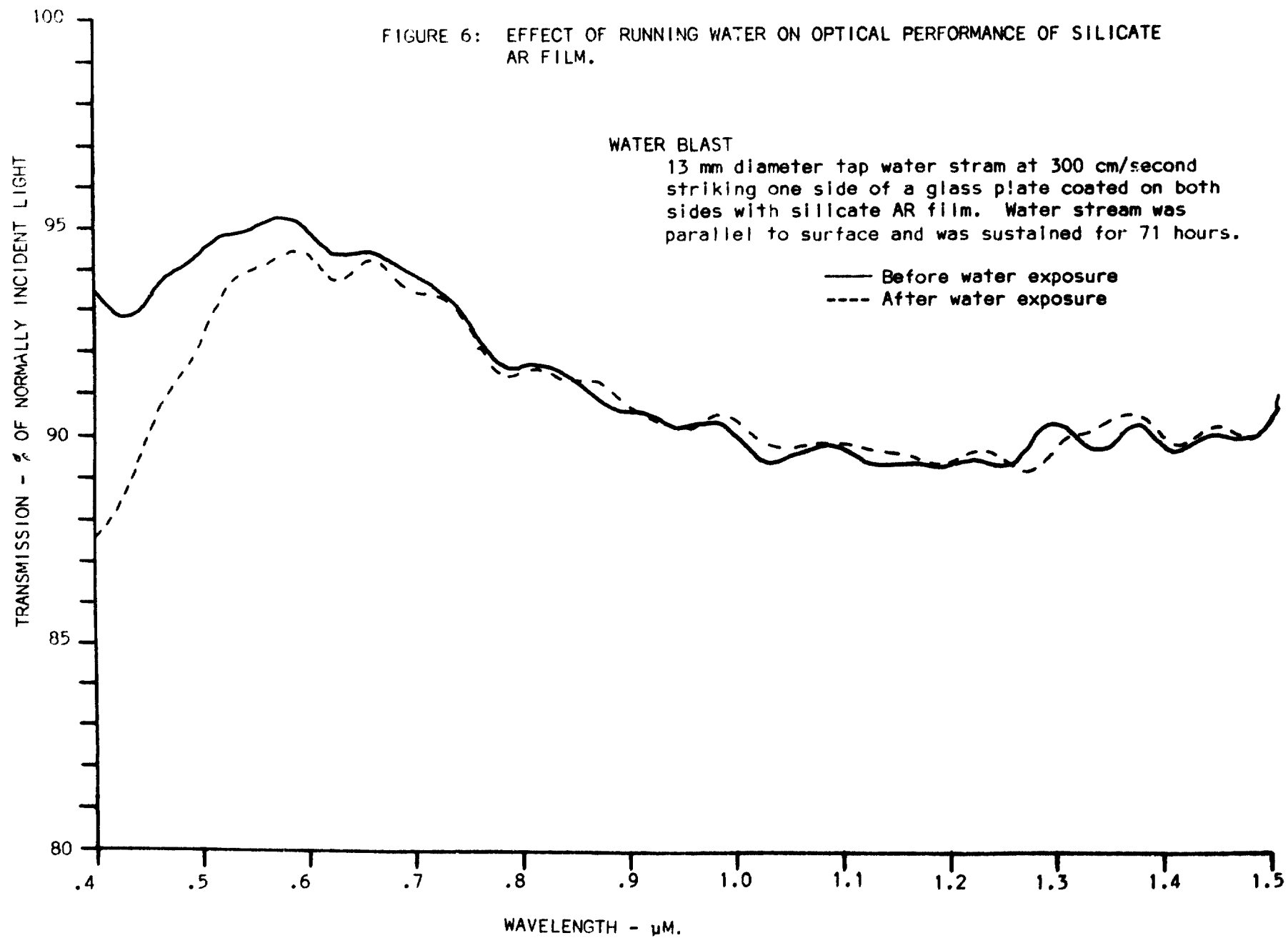
<u>FUME</u>	<u>EFFECT ON FILM</u>
Ammonia, dry	none
Carbon dioxide, dry	none
Hydrogen chloride, wet	none
Nitric acid vapor, wet	none
Nitrogen, dry (control)	none
Nitrogen dioxide, dry	slight brown stain; washed out with water.
Sulfur dioxide, dry	none

3.3.2.2 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.

<u>CLEANING AGENT</u>	<u>7 DAY EXPOSURE</u>	<u>30 DAY EXPOSURE</u>
Deionized water	no effect	no effect
Tap water	no effect	no effect
Jov Detergent (0.5 volume % in tap water)	no effect	no effect

FIGURE 6: EFFECT OF RUNNING WATER ON OPTICAL PERFORMANCE OF SILICATE AR FILM.



Isopropyl alcohol	no effect	no effect
Parson's clear ammonia	no effect	change of film color
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 partly of 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 no damage, exposures of over fifteen minutes' duration did remove film. 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, even though stain and soil removal can be accomplished, for the most part, with such mild cleansers as dish detergent.

3.3.2.3 WATER BLAST AND BOIL

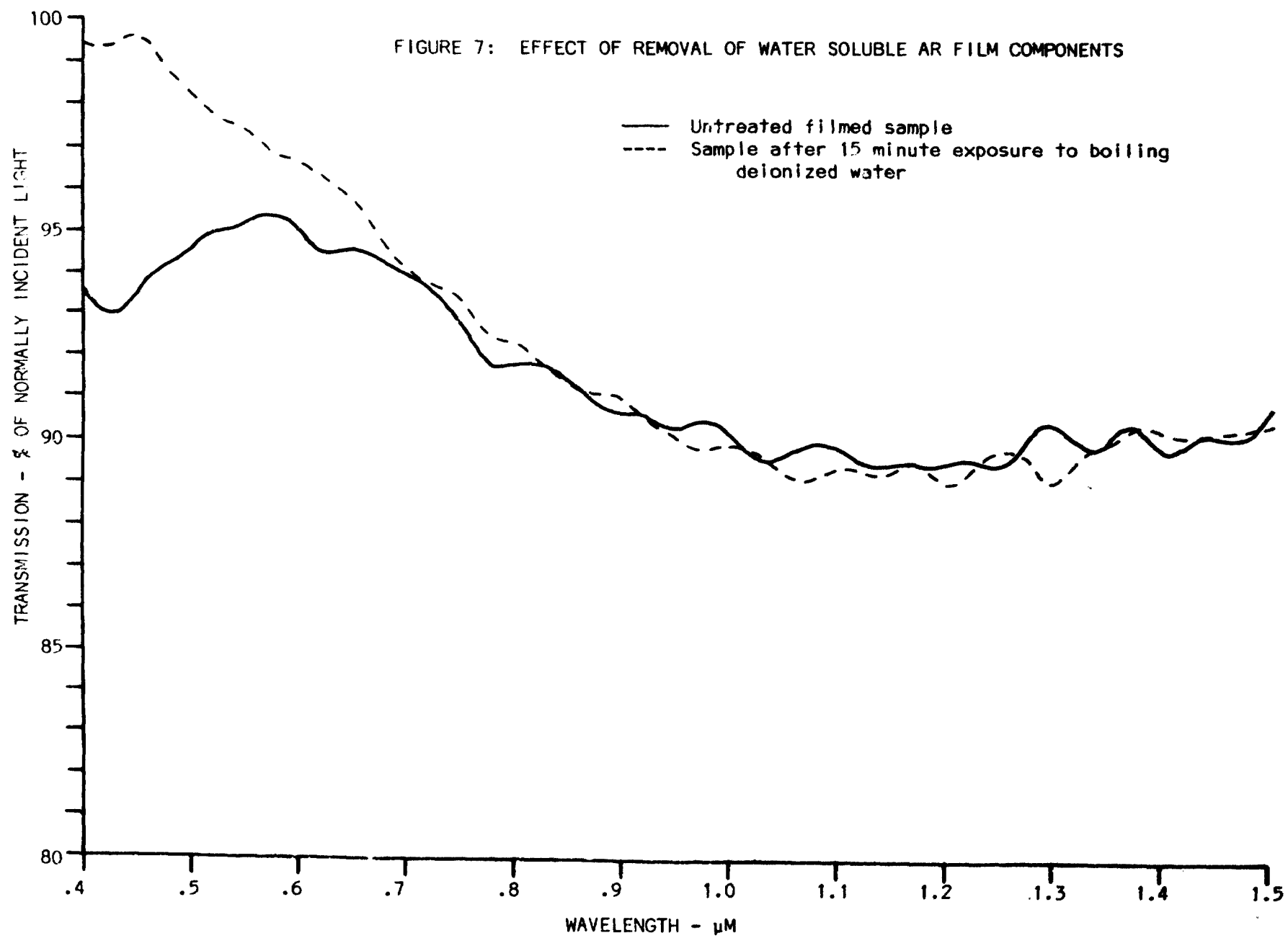
In order to simulate the exposure to heavy rain or an occasional cleaning with a spray from a garden hose that filmed module covers might face, a water blast was performed. In this severe test, a stream of rapidly moving tap water was directed downward at a filmed glass sample, striking the sample perpendicular 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 decrease in transmission in the wavelengths of the visible spectrum. (Figure 6).

It will be recalled from earlier discussions that the treatment of sodium silicate with sulfuric acid yields sodium sulfate in addition to silica,

so that the film consists, in part, of a water soluble component. The sodium sulfate is removed very slowly from the film by the action of cold water. In the water blast test above, the decrease in transmission of the film was evidently caused by a mechanism other than sulfate removal, since prolonged soaking in still or mildly agitated deionized water produced no comparable alteration of transmission properties. The removal of sulfate can be achieved rather quickly by boiling water. Figure 7 shows transmission results of a filmed plate (identical to that used for the water blast test) before and after exposure to boiling deionized water for fifteen minutes. (Before optical testing, the boiled filmed sample was dried for one week at room temperature and humidity in order to eliminate temporary transmission changes due to adsorbed water. This was also done in the case of the sample that underwent the water blast test.) Evidently the removal of sodium sulfate enhances the AR properties of the silicate film. The question arises as to whether the water blast test is a fair simulation of heavy rain and intentional rinsing and in what period of time the noted decrease in transmission will occur in the case of an actual solar module cover. Also in question is the length of time required for sodium sulfate removal with its attendant increase in transmission under actual conditions of use. More importantly, will sulfate removal cause an increase in transmission which compensates for the loss caused by water blasting? At present, very-long-term weather exposure data are not available to permit answers to these questions.

3.3.3 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.

3.3.3.1 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 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.

<u>STAIN</u>	<u>CLEANING REQUIRED</u>
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.

3.3.3.2 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 silicate AR filmed glass is the same as that of unfilmed glass.

3.3.3.3 SOOT

Because soot is a common atmospheric pollutant, and because of its opaque nature, module covers must be able to shed soot easily.

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.

3.3.3.4 FINGERPRINTS

Fingerprints deposited on silicate filmed glass do adversely affect the AR properties of the film, but to a lesser extent than they affect other types of AR coating. In any event, the hard, dense composition of the silicate film prevents penetration of the fingerprint liquids into the film. Both fresh and dried fingerprints were found to be easily removed by gentle wiping with 0.5% Joy detergent in water or by isopropyl alcohol.

4.0 CONCLUSIONS

1. The silicate method of forming AR films is capable of producing coatings of good optical performance (96.7% peak transmission at 0.540 μM wavelength as compared to 89.9% at the same wavelength for uncoated glass).
2. Processing conditions, such as solution concentration and withdrawal speed, can be varied easily so as to vary the wavelength of peak transmission and AR effectiveness of the film.
3. Stain and soil release properties are equivalent to those of uncoated glass. Soot release is uniformly better than uncoated glass.
4. Chemical resistance to gaseous air pollutants is excellent. Although the glass is attacked by some commercial cleaning agents, the stain and soil release properties of the coating make their use unnecessary. A mild dish detergent solution which the coating does withstand suffices for general cleaning.
5. The coating displays good mechanical abrasion resistance. Some instability is noted when the film is exposed to a water blast and to long-term sodium sulfate dissolution simulated by exposure to boiling water. In the former case, light transmission of filmed glass is reduced, while in the later, transmission is enhanced. In actual use, these effects may compensate for each other.
6. The process is very simple and reproducible. All operations are performed at room temperature. Only the provision of a dust-free dry atmosphere is necessary to assure film quality. The process is capable of scale-up to large scale production.

7. The process is inexpensive, using readily available and stable chemical reagents. The most expensive reagent used -- sulfuric acid -- may even be prepared on-site from sulfur trioxide or stack gas permitting further economy.
8. The process is largely independent of the substrate used. Nearly all types of glass can be treated, as well as those plastics that are hydrophilic and can stand brief exposure to concentrated sulfuric acid.

5.0 RECOMMENDATIONS

1. Further investigation of the possibility of increasing the optical performance of silicate films should be undertaken to further increase the attractiveness of the process. At present optical performance is good.
2. Data on the effects of long-term weather exposure is needed to permit analysis of the film's stability in actual use.

6.0 NEW TECHNOLOGY

This project sought to improve an existing concept -- the use of silicate coatings as antireflective films by introducing a convenient method of applying such films and regulating their thickness. In this case, the application method consists of constant speed withdrawal of the object to be coated from a liquid solution -- a process that is already in wide use in industry. The project has as its result the development of a process for the production of AR films, but the novelty of the technique lies in the combination of withdrawal and silicate coating rather than in the original development of either process. As such no new technology is reported.

7.0 COMPARISON OF METHODS

In a companion project (JPL Contract Number 955387), the production and testing of antireflective films by means of an acid leach process was studied. In this section, summarized results will be used to compare the advantages and disadvantages of the methods.

7.1 PRODUCTION OF ACID ETCHED AR FILMS

Acid etched AR films are produced when an acid solution selectively attacks the surface of soda-lime glass, dissolving and removing from a surface layer the calcium and sodium atoms that are normally present and leaving a skeleton of microscopically porous silica that has a refractive index that permits its use as an antireflective coating. Optical characteristics can be controlled by adjustment of the acid temperature, composition and duration of etch. The technique approaches the problem of forming a coating not by depositing anything, but rather by transforming a surface layer of the glass itself into an AR coating.

The process makes use of fluosilicic acid supersaturated with silica. Only at certain very narrow ranges of supersaturation will the acid leave the desired skeleton of silica. Therefore, the process is difficult to control, and is useful only on soda-lime glass. Moreover, fluosilicic acid is not a common industrial reagent and may pose problems of expense or lack of availability. The acid etched film also lacks durability.

In its favor, the acid etch technique is a physically simple process, requiring only a heated container and simple soaking of the glass to form an AR film. In addition, the optical efficiency of acid etched films is outstanding; AR coatings can achieve peak transmissions of 99.8% in the visible spectrum.

7.2 COMPARISONS

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

7.2.1 OPTICAL PERFORMANCE

Figure 8 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.

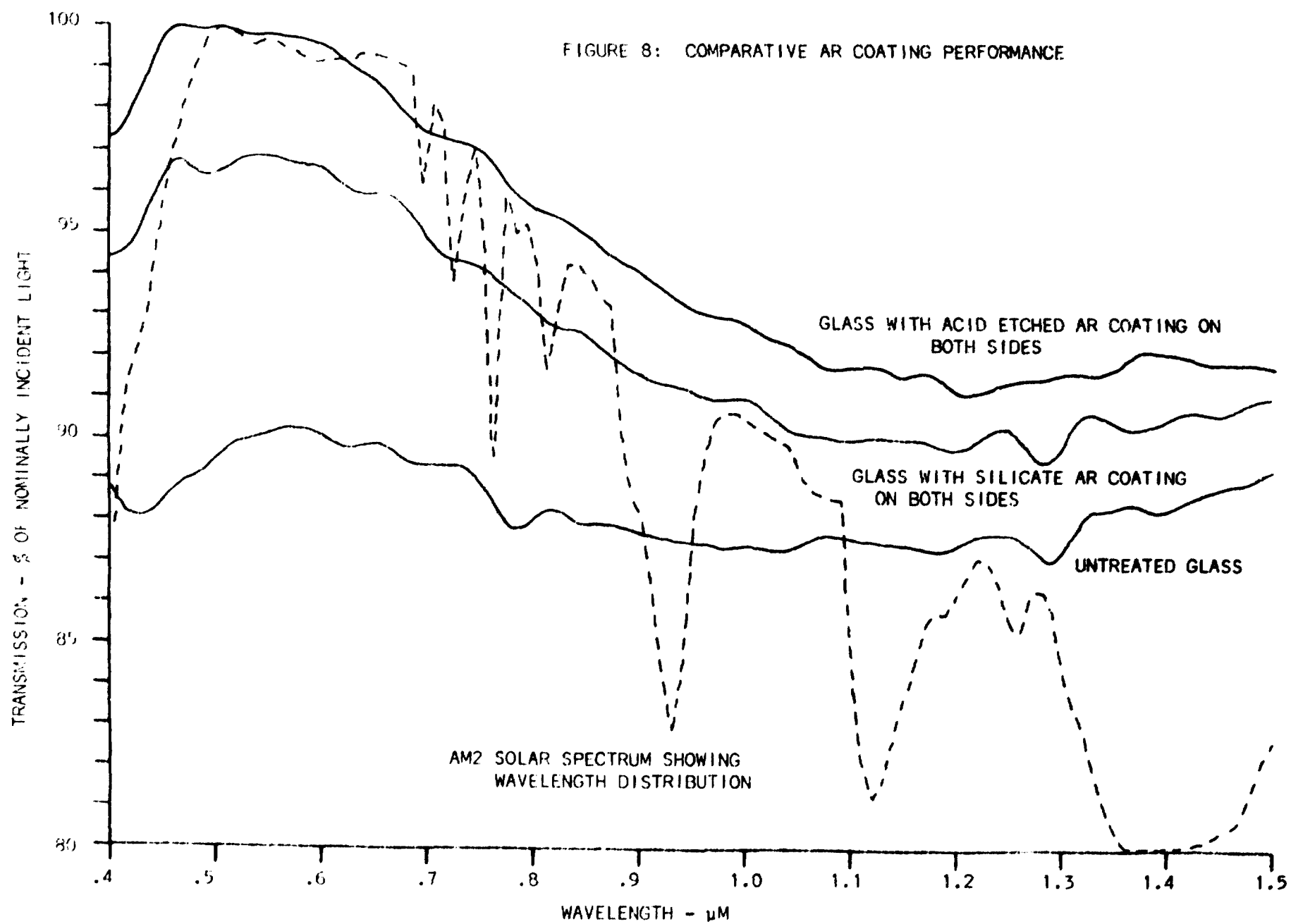
7.2.2 PROCESSING COMPARISON

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.



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

<u>STAIN</u>	<u>RESULT</u>
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.

<u>SOIL</u>	<u>RESULT</u>
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 as that of acid etched films. 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 9 shows the results of abrasion testing on silicate films, as well as on three different preparations of acid etched films. Silicate films are clearly superior in abrasion resistance.

7.2.7 SUMMARY

	<u>ACID ETCH PROCESS</u>	<u>SILICATE PROCESS</u>
Process Control	Very Poor	Very Good
Optical Efficiency	Excellent	Good

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

FIGURE 9
ABRASION TEST RESULTS

ABRASION PAD: 4 layers 0.008 inch cotton duck, 13.9 cm² area

PRESSURE: 138 G/cm²

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

8.0 REFERENCES

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