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LOW-COST SOLAR ANTIREFLECTION COATINGS

Semi-Annual Report, July 24, 1978—January 24, 1979

By
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MASTER

February 1979

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Honeywell, Inc.
Systems and Research Center
Minneapolis, Minnesota

U.S. Department of Energy

Solar Energy

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SEMI-ANNUAL REPORT

for the period 24 July 1978 - 24 January 1979

R.J.H. Lin, J.C. Lee and P.B. Zimmer

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February 1979

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The Solar Heating and Cooling
Research and Development Branch
Office of Conservation and Solar Applications
United States Department of Energy
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FOREWORD

This is the semi-annual report describing the work performed at Honeywell, Inc., Systems and Research Center, for U.S. Department of Energy under Contract No. EM-78-C-04-5300. The work has been supported by the Solar Heating and Cooling Research and Development Branch, Office of Conservation and Solar Applications, U.S. Department of Energy.

The authors acknowledge the guidance provided by Mr. Stanley W. Moore of Los Alamos Scientific Laboratory, the Project Monitor.

Dr. R.J.H. Lin is the Project Principal Investigator. The etched AR coating work was performed by Mr. J.C. Lee, Dr. R.J.H. Lin, and Ms. S.E. Heckler. The organic coating work was performed by Mr. P.B. Zimmer, Mr. W.D. McKelvey, Mr. G.W. Nelson, and Ms. W. Polec.

ABSTRACT

Production processes for low-cost organic antireflection (AR) coating and etched AR coating on glass are being developed and improved.

The etched AR coating process has been scaled-up to etch full-size glass panes but the chemical control of the etching solution remains a problem. Analytical methods including high performance liquid chromatography, flame exited atomic absorption and infrared spectroscopy, have been investigated as possible monitoring and control devices. Liquid chromatography appears to give some useful information. An investigation of another technique, utilizing the differential refractive index of the etching solution, has just begun.

The organic coating, FEP-120 Teflon dispersion, has been shown to be somewhat unstable and efforts are underway to improve the stability of the dispersion. A pretreatment of the glass substrate in hydrofluoric acid substantially improves the abrasion resistance of the coated glass. Further development will optimize this effect. Methods of maintaining thickness control during the coating of full size panels will be determined.

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SECTION I

INTRODUCTION AND SUMMARY

INTRODUCTION

The objectives of this program are to develop and improve production processes for two low-cost antireflection (AR) coatings for flat plate collector covers. An etched AR coating for glass panels is currently used on a manufacturing basis. Etching the glass panels reduces the solar reflection loss by 7%. The exterior durability, washability, and abrasion resistance of the coating is good (References 1 and 2) and the material and process costs are less than 20¢ per square foot. Control of the chemically complex etching solution is being investigated in this program, with the prime objective being the development of a fast and accurate method for monitoring and controlling the solution components during production runs.

The feasibility of AR coating FEP Teflon on glass has been demonstrated (Reference 1). Advantages of this organic coating include long term outdoor durability, solar transmittance increase of up to 5%, and material and process costs of less than 10¢ per square foot. The current efforts emphasize improving the handling durability of the coating and developing a method for maintaining thickness control in the process of coating full size glass panels.

SUMMARY

Etched AR Coatings

Three analytical methods have been utilized in the first six months' efforts to develop a feasible method of monitoring the glass etching process. High performance liquid chromatography, flame excited atomic absorption (AA), and infrared transmission spectroscopy were investigated as possible techniques. Chromatography seems to provide the most useful information but further development of the techniques involved is

necessary if this method is to be utilized in a manufacturing environment. Another approach, measuring the differential refractive index of the etchant has just been introduced to the study. This new method and chromatographic approaches will be developed in more detail during the final months of the program.

Organic AR Coatings

Progress is being made in the development of low cost, organic antireflection (AR) coatings used on glass solar collector windows. Etching the glass substrate in hydrofluoric acid significantly improves the abrasion resistance of the AR coating. The FEP-120 Teflon dispersion used to coat the glass is not totally stable as is evidenced by a reduced AR effectiveness in the coatings produced with aged dispersion. Additional work is needed to optimize the substrate etching conditions and stabilize the coating dispersion.

SECTION II

ETCHED AR COATINGS

GLASS ETCHING BATH

The nominal make-up of the glass etching bath (aqueous) is:

where the small quantities of boric or hydrofluoric acid are added as required to optimize the bath for a given set of etching conditions (solution temperature, agitation, bath loading, and etch time). (References 2-6.) Since commercial H_2SiF_6 is synthesized by dissolving hydrated silica in hydrofluoric acid,

the basic constituents are actually HF and $\text{SiO}_2 \cdot n\text{H}_2\text{O}$; thus the etchant recipe may be rewritten as:

So basically the etching bath as an aqueous solution of hydrofluoric acid saturated with dissolved glass which must be operated within a fairly narrow concentration range to impart an antireflected surface by selective removal at the alkali sites of common glazing soda lime sheet glass.

Note that while the etchant may be written as the sum of a few basic components, its dynamic equilibrium constituency is

1) Note that commercial hydrofluosilicic acid is available in aqueous solution ranging in assayed concentrations typically from 25 to 31%.

a complex mixture of fluorides, oxyfluorides, hydrofluorides, fluorosilicides, fluosilicates (and possibly fluoroborates) of the form:

Thus the problem of process monitor and control may be approached at several levels, from examining the details of the species heirarchy evolution down the equilibria chain, to simple solution physical properties characterization.

ANALYTICAL TECHNIQUES

Under a previous contract (Reference 1), preliminary studies of the etchant were made using gas chromatography, mass spectroscopy, and wet chemical techniques. During this period, high performance liquid chromatography (HPLC), flame excited atomic absorption (AA), infrared transmission spectroscopy, and differential refractive index measurements were the analytical methods surveyed for application to this problem.

Liquid Chromatography

The basic elements of a liquid chromatograph instrument consist of a liquid mobile phase (into which the sample to be analyzed is injected) which is pumped at a constant rate through a stationary phase (usually packed into a column) where the constituents of the sample are separated by differential retention affinity. The use of different physical mechanisms for the affinity of the sample to the stationary phase (e.g. hydrogen bonding, ion exchange, gel permeation, etc.) gives rise to the several types of liquid chromatography possible. The two types examined for application to the etchant bath problem were paired ion chromatography (PIC) and ion exchange/ion chromatography (IC).

Paired Ion Chromatography

The principles of this technique are schematicized in Figure 1.

Figure 1. Paired Ion Chromatography (PIC)

In classic liquid chromatography, separations are achieved using the differential affinity between the polarity of the sample in the mobile phase and a non-polar stationary phase. In PIC analysis, in which a highly polar electrolytic sample is to be separated, a polar stationary phase (just the opposite of the standard configuration, hence PIC is known as a reverse phase technique) is employed in conjunction with a reagent added to the mobile phase stream which equilibrates with the ion species (an anion for the etchant bath case) to be separated in such a way, as diagrammed,

non-ionic form of sample	non-ionic form of pairing reagent	
↑↑	↑↑	
ionic form of sample	ionic form of pairing reagent	pair/sample cation/anion

that the resultant pair reagent cation/sample anion product simulates a non-polar entity separable by a polar column in the normal manner.

As the various constituents of the sample elute from the analyzing column, they are monitored by UV transmission and deflection refractive index (DRI) detectors.

Chromatogram Development--The parametric variables in a PIC system include solvent polarity pH, type and concentration of the pairing reagent, and to an extent, the stationary phase.

To start with, a methanol/water system was used as the solvent, with tetrabutylammonium phosphate as the pairing reagent. Acetonitrile/water was also examined as a candidate solvent system.

In both cases a Micro-Bondapak C₁₈ column was used as the stationary phase (non-polar packing material treated with a monomolecular layer of octadecyltrichlorosilane) on a Waters Associates instrument package (pump and detector modules).

Two series of etchant samples were prepared for trial analysis, with known amounts of dissolved silica gel as determined gravimetrically by reacting the nominally 1.25 M H₂ Si F₆ solution with a known amount of silica gel, filtering the product to the 2 μm level on a Whatman 42 filter paper, ashing the filter/filtrate to a constant weight and subtracting from the original amount added.

As listed in Table 1, these solutions were doped to several potency levels (Appendix) by the appropriate boric or hydrofluoric acid additions and refiltered immediately to the 2 μm level (no attempt was made to recover and weigh any second stage filtrate).

Series I (1.90 g/l)

+ 10 potency units
0
0 diluted 15%
- 10
- 20
- 22

Series II (1.33 g/l)

+ 10 potency units
0
- 10
- 20
- 22

Table 1. Etchant Samples

These series of samples were used for several of the trial analytical techniques as will be discussed in more detail in the following pages.

PIC Chromatogram Baseline--Figures 2 and 3 are the baseline H_2O (50 μ l sample injections) chromatograms for the UV and DRI detectors respectively. Using a pump rate of 2 ml/minute (which was held constant throughout the PIC analysis), the baseline trace obtained, consists of a large main peak (with some fine structure on the leading edge) eluting at ~ 90 seconds, with some distinguishable minor bumps at ~ 120 and ~ 180 seconds.

PIC Sample Dilution Factor--Figure 4 shows the DRI chromatograms of samples I 0 and II 0 diluted 500/1 with water. The etchant DRI signature is simple, consisting of a relatively narrow negative peak eluting ~ 32 seconds after the main water peak, followed by a broader peak ~ 60 seconds later (labeled components A and B respectively, for convenience).

Figure 5 shows the DRI chromatograms of the same samples, only diluted 3/1 instead of 500/1. (Note that the signal scale is attenuated by a factor of 1/1600 for these scans.) The same post H_2O spike signature peaks appear, only much broadened with some indication of farther fine structure, plus the appearance of a sharp negative peak just before the water spike. Since the 500/1 dilution factor was particularly convenient for companion atomic absorption determinations, most of this preliminary PIC analysis was done at this dilution factor.

Figure 2 H₂O Baseline (UV Detector).

Figure 3 H₂O Baseline (DRI Detector)

sample I 0
500/1 dilution
50 μ l injection

DRI
signal

sample II 0
500/1 dilution
50 μ l injection

Time 2 minutes/inch

Figure 5. PIC DRI Chromatograms at 2/1 Dilution

Figure 6 shows the DRI chromatograms for the series I samples diluted 500/1; similarly, Figure 7 gives the UV chromatograms for this same series of samples. Note that the UV etchant signature is qualitatively very similar to the DRI trace, consisting of a narrow peak (component A) eluting ~ 32 seconds after the H₂O spike, followed by a broader peak ~ 60 seconds later. Except for relative peak heights, Figure 8 shows there is no fundamental difference between the PIC UV chromatograms of the series I and II samples.

Solvent System Effects--Figure 9 illustrates the effect of varying solvent composition on the chromatogram development; namely, the higher the ratio of the MeOH in the solvent, the faster the component elution rate. Note how the fine structure on the leading edge of the water spike is resolved by using the 40/60 MeOH/H₂O solvent ratio.

Figure 10 compares PIC UV chromatograms developed in MeOH/H₂O with those done with an acetonitrile/H₂O solvent system. The acetonitrile/H₂O signature exhibits considerably less structure.

Ion-Exchange/Ion Chromatography (IC)

The principles of this technique are schematicized in Figure 11. As given in Figure 11, a carbonate/bicarbonate solution is used as the mobile phase. This system is used because the carbonate and bicarbonate are relatively easily neutralized to low conductivity species, and the different combinations of $\text{CO}_3^{2-}/\text{HCO}_3^-$ act to buffer the pH. This allows separations over a large range of affinity.

DRI
signal

I +10

I 0

I -20

I 0 15%

I -10

I -22

Time 2 minutes/inch

Figure 6. PIC DRI Chromatograms

UV
signal

I +10

I 0

I -20

I 0 15%

I -10

I -22

Time 2 minutes/inch

Figure 7. PIC UV Chromatograms

sample I 0
500/1 dilution
50 μ l injection

UV
signal

component A

sample II 0
500/1 dilution
50 μ l injection

Time 2 minutes/inch

Figure 8. PIC UV Chromatograms

UV
signal

40/60 MeOH/H₂O
sample II -22

50/50 MeOH/H₂O
sample II -22

Time 2 minutes/inch

Figure 9. PIC UV Chromatograms
Solvent Polarity Effects

UV
signal

Time 2 minutes/inch

Figure 10. PIC UV Chromatograms
Solvent Polarity Effects

Sample in
carbonate/bicarbonate
mobile phase

suppressor column
strong cation
exchange resin (R)

Function: HCO_3^- and
 CO_3^{2-} removal

and

Separator Column
Low capacity anion exchange resin

Conductimetric detector

H-A's detected with dissociation
constants $K_{\text{HA}} \geq K_{\text{H}_2\text{CO}_3} \sim 10^{-7}$

Figure 11. Ion Exchange/Ion Chromatography (IC) Anion Analysis Scheme

The first exchange column has two functions: 1) to convert the unknown A anion species to the acid form H-A and 2) to suppress the highly conducting $\text{CO}_3^{2-}/\text{HCO}_3^-$ background by conversion to H_2CO_3 ; thus the unknown (in the form H-A) may be presented to the second analyzer column in a very low conductivity background, considerably increasing the detector sensitivity over conventional single column ion exchange systems.

This technique was recently developed by Small et. al. (Reference 7) of Dow Chemical and commercial instrumentation based on this has been marketed for about a year by Dionex Corporation (Reference 8) a subsidiary of Dow.

Arrangements were made with Dionex to analyze etchant samples in their applications laboratory with the following results:

IC Cation Analysis--The scans revealed no unexpected cations present, i.e., given the bath composition, H^+ is the only likely cation (except for some anomalous fast eluting contamination peaks due to shipping container problems).

IC Anion Analysis--Figure 12 is the chromatogram of a standardizing solution of known composition used to calibrate the instrument. Figure 13 gives the anion IC chromatogram of a 0 potency etchant sample diluted 500/1. Four peaks are resolved, two of which may be readily identified by reference to the calibration scan. The large peak eluting first is most likely F^- or F^- in combination with SiF_6^{-2} . The small peak eluting last is probably SO_4^{-2} (at the 700 ppm level) due to impurities in the starting reagents. Since the other two peaks do not directly match any of Dionex's other known standards (one of them may be PO_4^- , as indicated in Figure 12), they would have to be identified by other means.

The IC chromatograms for etchant samples doped to various potency levels are essentially identical, except for relative peak height variations, just as was observed for the PIC chromatograms.

By referencing to the peak height of an F^- standard of known concentration, the F^-/SiF_6^{-2} peak may be quantitatively determined. These measurements for the series I and II samples are given in Table 2.

2) Because of the equilibrium

there is no way of knowing whether this peak represents F^- only or a combination of F^- and SiF_6^{-2} .

Sample	(F ⁻) in %	(F ⁻) in M/l ³
I 0	15.4	8.106
I +10	14.1	7.422
I 0 15%	12.8	6.737
I -10	14.5	7.632
I -20	14.3	7.527
II 0	14.9	7.843
II +10	15.0	7.895
II -10	14.8	7.790
II -20	14.6	7.685
II -22	14.5	7.632

Table 2. F⁻ as Determined by IC

3) Conversion factors: 1% = 10⁴ ppm where 1 g/l = 1000 ppm
 since 1 mole of F⁻ 19 g, (F⁻) in M/l = (F⁻) in % x 10 ÷ 19.

Figure 12. IC Standard Anions

Figure 13. IC Etchant Chromatogram

Note, because of the extreme sensitivity of the technique, the etchant samples were diluted 50,000/1 to obtain these results.

Atomic Absorption

A schematic of the atomic absorption apparatus⁴ is given in Figure 14.

Figure 14. Atomic Absorption Apparatus

As diagrammed, the UV transmission at a characteristic Si emission wavelength (produced by a hollow cathode discharge lamp) is measured for a liquid sample thermally plasma fragmented by flame excitation. By referencing to the transmission of standardized samples of known concentrations, the elemental silicon concentration of the etchant may be determined. The measurements for series I and II samples are given in Table 3.

Sample	ppm Si as diluted (500/1)	g/l Si Original	M/l Si Original
I 0	104.8	52.4	1.86
I +10	90.2	45.1	1.60
I 0 15%	96.7	48.4	1.72
I -10	107.1	53.6	1.91
I -20	98.0	49.0	1.74
II 0	93.1	46.6	1.66
II +10	100.7	50.4	1.79
II -10	94.4	47.2	1.68
II -20	91.0	45.5	1.62
II -22	91.7	45.9	1.63

Table 3. (Si) as Determined by Atomic Absorption

4) The actual instrument used was a Perkin-Elmer 603

Infrared Spectroscopy

Using a liquid cell improvised from an ordinary polyethylene sheet (~ 2 mils thick) bag (see Figure 15), infrared transmission scans of the full strength etchant were made on a Beckman 4240 IR spectrophotometer from 2.5 to 40 microns. As indicated in Figure 16, this somewhat crude technique reveals significant differences in transmission away from the strong water bands at 2.9 and 6.2 microns for samples doped to various potency levels. These differences appear to be due to scattering from precipitate formed from solution in the cell, which makes the data highly dependent on the sampling technique and thus very difficult to quantitate consistently. Note that the fairly close coincidence of the strong water band minima indicates the improvised cells' thicknesses to be fairly uniform.

Figure 15. Baggie Liquid Cell

Differential Refractive Index

It seems evident that a major determinant of the AR etchant bath efficacy is the total amount of silica reacted in the liquid phase of the etchant. This information may be more easily extracted from direct physical characterizations of the etchant solution, than by more involved chemical analytical methods, and it seems appropriate to initiate work in this direction.

One approach is to measure the index of refraction of the etching solution as a function of gravimetrically determined silica concentrations and etchant potency variations. This may be done with the differential refractive index cell diagrammed in Figure 17, using a laser to achieve the necessary optical leverage

Figure 16. Etchant IR Transmission

required to measure $\Delta x/L$ with sufficient precision, where:

from Snell's Law $\sin \alpha_1 / \sin \alpha_2 = n_2 / n_1$ and

trigonometry $\phi = \alpha_1 - \alpha_2$

and $\sin x + \sin y = 2 \sin ((x+y)/2) \cos ((x-y)/2)$

algebraic manipulation gives

$$\frac{n_2}{n_1} \sin \alpha_2 = 2 \sin(\phi/2) \cos((\alpha_1 + \alpha_2)/2) + \sin \alpha_2$$

For $n_2 = n_1 + \Delta n$, $\Delta n/n \ll 1$, $(\alpha_1 + \alpha_2)/2 \sim \alpha_1$

this reduces to

$$\phi \sim (\Delta n/n_1) \tan \alpha_1$$

and choosing $\alpha_1 = 45^\circ$ gives

$$\phi \sim \Delta n/n$$

Now on exiting the cell, the beam is refracted an additional amount ψ , where from Snell's law

$$n_2 \sin \phi = \sin(\phi + \psi) \text{ and since}$$

$$n_2 = n_1 + \Delta n \text{ and } \sin \phi \sim \phi \sim \Delta n/n, \sin(\phi + \psi) \sim (\phi + \psi)$$

gives $(\phi + \psi) \sim (n_1 + \Delta n) \Delta n / n_1$ or finally

$$\Delta x/L \sim \Delta n_1 (1 + \Delta n/n_1)$$

Figure 17. Differential Refractive Index Cell

DATA ANALYSIS

PIC Data

The normalized peak heights of component A (A peak height divided by water spike height normalized to the smallest ratio value) as given in the PIC chromatograms of Figures 6 and 7, are plotted in Figure 18 as a function of potency. The data indicates the concentration of the A component to be an increasing function of potency. (The inconsistency of the -20 UV data is unexplained.)

IC Data

The fluoride ion concentration data of Table 2 is plotted as a function of potency in Figure 19. The data indicates even for potencies less than zero, (F^-) to be an increasing function of potency. (The inconsistency of the I +10 point is unexplained.) Also notice that the concentrations of F^- determined by this method (the average(F^-) from Table 2 is ~ 7.7 m/l) are very close to the nominal 7.5 m/l expected from the basic etchant make-up recipe as listed on page 10. Considering the extreme dilution factor involved (50,000), this agreement, and the general consistency of the data is remarkable.

AA Data

The elemental Si concentration data given in Table 3, is plotted as a function of potency in Figure 20. Note that this data is very noisy, both because of intrinsic instrumental limitations (flame flicker) and the problems encountered in maintaining the etchant sample in single liquid phase throughout these measurements; however the general trend of the data indicates (Si) to be an increasing function of potency also.

IR Transmission Data

As previously discussed, the technique is too sample dependent to draw consistent quantitative data from; however, qualitatively it was observed, the lower the potency, the more precipitate seemed to form.

Figure 18. Normalized $\square A$ vs Potency for Series I samples via PIC

Figure 19. $[F]$ vs Potency via IC

Figure 20. $\boxed{S1}$ vs Potency
via AA

Discussion

All the data clearly indicates the effect of boric acid additions to the bath (i.e., lowering the potency) is to push the equilibrium chain in the direction that phase separation occurs (i.e., the glass saturation capacity of the etchant is lowered). Both Si and F^- are removed from the etchant, which suggests the formation of some form of oxyfluoride glassy gel precipitate.

By graphically averaging the data as indicated in Figure 21, with the "best" fit straight lines, the determined F/Si ratio is very close to 3/1. Listing the possible oxyfluorides⁵ in Table 4, the most likely candidate is Si_2F_6O .

	F/Si
SiF_2O	2
Si_2F_6O	3
$Si_2F_4O_2$	2
$Si_2F_2O_3$	1
$Si_3F_{10}O$	10/3
$Si_3F_8O_2$	8/3
$Si_3F_6O_3$	2
$Si_3F_4O_4$	4/3
$Si_3F_2O_5$	2/3

Table 4. Oxyfluoride Stoichiometry

5) via: $pSiO_2 + 2(2p - q)HF \rightleftharpoons Si_pF_{2(2p - q)}O_q + (2p - q)H_2O$
 where p, q integers, $2p - q > 0$

slope $\sim .069$ m/l Si per PU

slope $\sim .20$ m/l F per PU

$\frac{[F]}{[Si]}$ ~ ratio
of
slopes
 ~ 2.95

Figure 21. Graphical Average Stoichiometry Determination

SECTION III

ORGANIC AR COATINGS

This work is a continuation of earlier efforts (reference 1) in which the feasibility of fused fluorocarbon dispersion AR coatings on glass was demonstrated.

REPEATABILITY

A series of tests were performed to verify the effects of certain parameters of the coating process on transmittance. Dip coating rate and coating solids content were the parameters selected for study.

FEP-120 Teflon dispersion is received from Dupont at 52% solids and is diluted to 8% with dionized water. Glass substrates were cleaned by soaking in chromic acid for approximately 16 hours, rinsed with deionized water, blown dry with nitrogen and baked at 200°F for one hour. After cooling to room temperature, the glass substrates were measured for transmittance from 0.35 to 0.75 μ m using a Beckman DBG spectrophotometer with an integrating sphere.

Cleaned glass substrates were coated with 8% solids FEP-120 Teflon dispersion at dip coating rates of 2 to 20 inches per minute. The substrates were air dried 30 minutes at room temperature, force dried 60 minutes at 250°F, and then exposed to 775°F for 10-15 minutes to fuse the fluorocarbon particles. After cooling slowly (to avoid cracking) to room temperature, the transmittance of the now coated glass was remeasured.

The difference between the transmittance before and after coating was calculated, adjusted to solar weighted (air mass = 2) values, and plotted as a function of dip rate in Figure 22.

The transmittance increase was greater at slower dip rates (i.e., 2 to 4 in./min.) than at faster dip rates (i.e., 6 to 20 in./min.) as shown in Figure 22. This data verified earlier results.

Another set of experiments was done to provide data on the effect of coating solids on transmittance increase. The FEP-120 Teflon dispersion was diluted to 2 to 30 percent solids with deionized water. Coatings were made on glass substrates at 2 in./min. and 4 in./min. dip coating rates, cured, and measured as before. The increase in solar transmittance was plotted as a function of coating solids on Figures 23 and 24 for dip coating rates of 2 in./min. and 4 in./min., respectively.

Figures 23 and 24 illustrate the satisfactory correlation of the transmittance characteristics of samples run during the feasibility study in a previous program (Reference I) and samples prepared recently. A new dip coater allowed for greater control of the dipping process in preparation of the current samples. This control improvement can be expected to result in more accurate data. The figures show that a more transparent coating is produced at a dip rate of 2 in./min. and that the optimal range of dispersion solids is from 4 to 12 percent. Transmittance increases of as much as 4.7-4.9 percent have been achieved using the FEP-120 Teflon dispersion and a 2 in./min. dip rate.

During this phase of investigation it became apparent that, as the FEP-120 Teflon dispersion aged, glass substrates coated with it showed smaller increases in transmittance. A systematic purchase of one new batch of dispersion per month was initiated. Aged dispersion was periodically checked by measuring transmittance increase when applied to glass substrates. The details of this investigation are reported under "Solution Stability" of Section 3.

Figure 22. Solar Transmittance Increase of Glass, Dipcoated at various Withdrawal Rates in 8 % solids FEP-120 Teflon Dispersion

Figure 23. Solar Transmittance Increase of Glass
Dipcoated at a 2 in/min Withdrawal Rate

Figure 24. Solar Transmittance Increase of Glass Dipcoated at a 4 in/min Withdrawal Rate

IMPROVEMENT OF ABRASION RESISTANCE

The FEP-120 Teflon dispersion applied directly to glass is easily damaged by handling. An effort has begun to minimize damage due to handling by improving abrasion resistance. Initial development concentrated on increasing the surface area of the glass substrate through etching in hydrofluoric acid solutions.

Hydrofluoric acid concentrations from 0.01 to 5 percent with glass exposure times from 30 seconds to 5 minutes were used. Glass substrates were coated with 8 percent solids FEP-120 Teflon dispersion at 2 in./min., the coating fused and transmittance measured before and after exposure to abrasion. The abrasion test consisted of rubbing the coated glass with cheesecloth under 0.7 psi for 100 cycles. The results are shown in Table 5.

Table 5 does not show any definite pattern or trend. The only information from Table 5 which indicate a somewhat inconsistent pattern was that some samples etched more deeply (i.e., longer time at low concentrations or short time at higher concentrations) had an increase in transmittance after the abrasion test.

Because the lack of specific pattern from the data in Table 5, a second test was conducted to better define the effect of etching glass on the abrasion resistance of the FEP-120 Teflon coating. Hydrofluoric acid concentrations were maintained at 0.01 to 5 percent and glass immersion time from 0.5 to 5 minutes. FEP-120 Teflon dispersion at 10 percent solids was dip applied at 2 in./min., air dried and fused as before. Transmittance was measured before and after abrasion exposure and are shown in Table 6.

From Table 6 it seems that as the time of etching or concentration of hydrofluoric acid increases, a specific etched quality of the glass substrate can be achieved which results in coated panels that are abrasion resistant (i.e., transmittance of sample does not change after abrasion test). In certain samples the transmittance increased after exposure to abrasion. Further testing is needed to reproduce and substantiate these results. SEM will be used to examine the effects of varying acid concentration and

Table 5. Solar Transmittance of Etched Glass Coated with FEP Teflon Before and After Abrasion Exposure

Etching Condition		Solar Transmittance (%)		
CON	CN (%) Time (Min)	Before	After	Difference
0	0	94.2	92.6	-1.6
0.01	0.5	95.3	94.1	-1.2
0.01	1.0	94.4	92.8	-1.6
0.01	3.0	94.9	92.9	-2.0
0.01	5.0	93.8	93.2	-0.6
0.1	0.5	93.8	92.5	-1.3
0.1	1.0	94.4	93.1	-1.3
0.1	3.0	94.3	95.6	+1.3
1.0	0.5	94.7	93.3	-1.4
1.0	1.0	94.6	94.8	+0.2
5.0	0.5	94.4	95.1	+0.7
5.0	1.0	93.2	94.5	+1.3

8% solids, coated at 2 in./min.

Table 6. Solar Transmittance of Etched Glass Coated with FEP Teflon Before and After Abrasion Resistance

Etching Condition		Solar Transmittance (%)		
CON	CN (%) Time (Min.)	Before	After	Difference
0	0	93.5	92.9	-0.6
0.01	0.5	94.2	93.7	-0.5
0.01	1.0	94.5	93.7	-0.8
0.01	3.0	94.0	93.6	-0.4
	5.0	93.0	93.0	0.0
0.1	0.5	93.6	93.1	-0.5
	1.0	94.3	93.4	-0.9
	3.0	93.2	93.5	+0.3
1.0	0.5	93.3	93.5	+0.2
	1.0	93.7	93.7	0.0
5.0	0.5	93.5	93.6	+0.1
5.0	1.0	93.7	93.7	0.0

10% Solids, coated at 2 in./min.

etching time on surface characteristics.

SOLUTION STABILITY

During the early part of this development effort, it became apparent that the FEP-120 Teflon dispersion was changing in a manner that adversely affected its AR characteristics. The dispersion as received from the vendor is at 52% solids and must be reduced to 8-10% solids for dip coating glass. It wasn't clear at the time nor is it now what is taking place in the dispersion to cause reduced transmittance on glass. As a result of this problem new material is ordered each month to maintain a fresh stock and old material is periodically used for coating and transmittance increase is monitored. Table 7 shows the results of monitoring to date and Figure 25 provides a graphical representation of two lots of Teflon dispersion applied at 8% solids that can be validly compared.

From Table 7 it can be seen that lot 762 provides an increased transmittance of 4.7% when evaluated four weeks after receipt from the vendor. One week later this same lot of coating dispersion resulted only 4.2% increased transmittance, a drop of 0.5%. Seventeen weeks after receipt, the same lot of material showed 3.1% increased transmittance on glass, a drop of 1.6% from that of the coating made four weeks after receipt. The test was repeated to the extent of available aging data for lot 791 "A". Results can better be seen in Figure 25.

The vendor recommends periodic agitation of the dispersion on a weekly basis to maintain its uniformity. Although there was no scheduled agitation of lots 762 and 791 "A", the dispersions were agitated prior to each use. As the data in Table 7 and Figure 25 show, this agitation failed to alter the degradation of the dispersion for AR coating purposes.

Table 7. Transmittance Increase of Glass Coated with FEP-120 Teflon Which Has Been Aged for Various Lengths of Time.

Lot Number	Coating Solids (%)	Weeks After Receipt	Transmittance Increase (%)
762	8	4	4.7
		5	4.2
		17	3.1
	10	10	3.7
		12	3.0
791 "A"	8	15	3.0
		4	4.9
791 "B"	8	6	3.9
		1	3.5

Lot 791 "B", which was ordered after lot 791 "A", was evaluated immediately after receipt and shows transmittance increase of 3.5%. The "A" and "B" designations were arbitrarily assigned to distinguish between two shipments of the same lot of dispersion. Presumably lot 791 "B" was properly agitated by the vendor prior to shipment, yet shows significantly lower transmittance increase than the same lot of material shipped earlier. The results of lot 791 "B" are shown in Table 7. Although the data in Table 7 is somewhat incomplete it does suggest that the lower limit of the transmittance increase produced by a coating of aged material is about 3%. Whether this is, in fact, true will be determined through further evaluation of the dispersion. With 3% increased transmittance, the FEP-120 dispersion at an estimated material cost of less than 1¢/ft² remains a viable low cost AR coating.

It should be noted that the use of FEP-120 Teflon dispersion as an AR coating for glass is probably unique. The vendors experience with the material must therefore be taken in this perspective. Further discussions with the vendor will be undertaken to bring to bear their technology in solving the stability problem.

Figure 25. Solar Transmittance Increase of Glass Coated with Aged FEP-120 Dispersion

FUTURE PLANS

ETCHED AR COATINGS

Of the analytic techniques surveyed for application to AR glass etching process monitor and control, the chromatographic and refractive index measurement approaches are the most promising; these approaches will be developed in more detail during the remainder of the program.

ORGANIC AR COATINGS

Future plans include the following:

- 1) Continue the investigation of etching conditions including hydrofluoric acid concentration and glass exposure time for coating abrasion resistance optimization.
- 2) Continue monitoring the transmittance decrease of aging FEP-120 Teflon dispersion. Investigate the cause of the decrease using SEM, sedimentation, or other analytical procedure.
- 3) Initiate long term humidity and accelerated weathering exposure tests for organic AR coated etched and unetched glass.
- 4) Scale up and coat a large (3 ft x 6 ft) glass panel using the optimized process.

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APPENDIX

SOLUTION POTENCY OF GLASS ETCHING BATH

The term "potency" was first used by Thomsen¹ to describe the degree of supersaturation in a silica supersaturated fluo-silicic acid solution. It determines the vigor of the acid attack on silica and, similarly, on glass. The potency number is an arbitrary unit and zero value of potency is arbitrarily assigned to the silica-saturated acid as a reference. A one milliliter addition of 4 percent boric acid per liter of silica-saturated acid solution diminishes the potency by 2 units and results in a super-saturated solution, i.e., the solution potency has been changed from zero to -2. The addition of one milliliter of 3-molar potassium fluoride per liter of silica-saturated acid solution increases the potency by 2 units and results in an unsaturated solution, i.e., a potency change from zero to +2. A negative potency number indicates a higher degree of supersaturation, e.g., a potency of -20 signifies a higher degree of supersaturation than a potency of -18.

¹See Ref. (Section 2)