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LOW-COST SOLAR ANTIREFLECTION COATINGS

Annual Report for July 24, 1978—September 24, 1979

By
R. J. H. Lin
J. C. Lee
P. B. Zimmer

October 1979

Work Performed Under Contract No. EM-78-C-04-5300

Honeywell, Inc.
Systems & Research Center
Minneapolis, Minnesota

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Solar Energy

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ANNUAL REPORT

For the Period 24 July 1978 - 24 September 1979

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October 1979

Prepared for

Solar Heating and Cooling Research and Development Branch
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FOREWARD

This is the annual report describing the work performed at Honeywell, Inc., Systems and Research Center, for U.S. Department of Energy under Contract No. DE-AC04-78CS35300. 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.

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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 pressure liquid chromatography (HPLC), flame excited atomic absorption, infrared spectroscopy, Coulter counter techniques, and liquid index of refraction measurements were examined for application to this process monitor and control problem. A phenomenological model for the key reaction species in the etching process is presented along with a monitor control scheme using refractive index measurements to set the initial reactant concentrations and HPLC to track in-process concentrations.

The environmental durability of the organic AR coating of fused FEP-120 Teflon dispersion has been improved by the use of a hydrofluoric acid etch/silane coupling agent pretreatment. Improved coating processing techniques were developed culminating in the demonstration of scale-up feasibility for this process for glass panels up to 1 ft by 1 ft with good batch sample to sample repeatability.

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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 was investigated in this program, with the prime objective being the development of fast and accurate methods 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 effort emphasized improving the handling and environmental 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

Several analytic methods including high pressure liquid chromatography, flame excited atomic absorption, infrared spectroscopy, Coulter counter techniques and liquid index of refraction measurement techniques were evaluated as means of monitoring the glass etching process. In summary, the technical accomplishments of this work include:

- The development of analytic methods for improving large-scale AR glass process control. Differential refractive index measurement can be used to quickly and accurately determine the initial etchant concentration and chromatographic techniques can be used to monitor the etching solution during the etching process.
- The identification of the role of the particulate/colloid nature of the etchant in determining the process equilibrium operating point.
- The development of a phenomenological model for the process key reaction species incorporating the role of the etchant colloid phase.

Organic AR Coatings

In summary, the technical accomplishments of this work include:

- The demonstration of scale-up feasibility for this process for glass panels up to 1 ft by 1 ft with good batch sample to sample repeatability.
- The marked improvement in coating durability made possible by a glass etch/silane coupling agent pretreatment processing step.

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 reacting hydrated silica with 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 etchant bath is 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.

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

Note that while the etchant may be written as the sum of a few basic components, its dynamic equilibrium constituency is a complex mixture of fluorides, oxyfluorides, hydrofluorides, fluorosilicates (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. In this work, high pressure/performance liquid chromatography (HPLC), flame excited atomic absorption (AA), infrared transmission spectroscopy, differential refractive index measurements, and particle size distribution determination via Coulter counter techniques 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:

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 reacted silica gel as determined gravimetrically by reacting the nominally 1.25 M H₂SiF₆ 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)	Series II (1.33 g/l)
+ 10 potency units	+ 10 potency units
0	0
0 diluted 15%	- 10
- 10	- 20
- 20	- 22
- 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 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 H_2O 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

Figure 2 H₂O Baseline (UV Detector)

Figure 3 H₂O Baseline (DRI Detector)

DRI
signal

Figure 4. PIC DRI Chromatograms

Figure 5. PIC DRI Chromatograms at 2/1 Dilution

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

Figure 7. PIC UV Chromatograms

UV
signal

water peak

component A

sample I 0
500/1 dilution
50 μ l injection

sample II 0
500/1 dilution
50 μ l injection

Time 2 minutes/inch

Figure 8. PIC UV Chromatograms

UV
signal

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

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.

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 $K_{\text{HA}} \gg K_{\text{H}_2\text{CO}_3} \sim 10^{-7}$

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} .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.

²Because of the equilibrium

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

Figure 12. IC Standard Anions

Figure 13. IC Etchant Chromatogram

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.

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.

³The actual instrument used was a Perkin-Elmer 603

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

⁴Conversion 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.

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

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

Clearly, 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.

One approach is to correlate the index of refraction of the etching solution to constituent concentrations and potency variations. This may be done with the differential refractive index cell diagrammed in Figure 17, using a laser

Figure 16. Etchant IR Transmission

Figure 17. Differential Refractive Index Cell

to achieve the necessary optical leverage⁵ 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 $\phi = \alpha_1 - \alpha_2$

$$\text{and } \sin x \pm \sin y = 2 \sin ((x \pm y)/2) \cos ((x \mp y)/2)$$

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

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

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

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

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

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

⁵Besides the optical lever readout scheme described here, recently both holographic and interferometric techniques have been used to measure liquid refractive indices with comparable precision to the method described above, as reported by

B. Beysens, "Simple, Reliable, and Sensitive Interferometer for the Measurement of the Refractive Index of Liquids as a Function of Temperature," Rev. Sci. Instrum., 50, 509 (1979)

D.H. McQueen, "Holographic Refractometer," J. Phys. E:Sci. Instrum., 12, 111 (1979)

A differential refractive index cell with 100 cc compartment capacity (in the general configuration of Figure 17) was constructed out of etchant resistant plexiglass.⁶ A Lauda circulating water bath was used to thermostat the cell and a small Spectra-Physics He-Ne alignment laser was used to complete the apparatus. Using deionized water as the primary reference standard, the apparatus was calibrated using tabulated index⁷ values for sucrose solutions of known concentrations. These data are given in Table 4 and Figure 18.

Percent sugar		0	1	2	3	4	5	6	7	8	9
00.	1.3	330	331	333	334	336	337	338	340	341	342
1.		344	345	347	348	350	351	353	355	356	357
2.		359	361	362	363	365	367	368	369	371	373
3.		374	375	377	378	380	381	382	384	385	387
4.		388	389	391	393	394	395	397	399	400	401
5.		403	405	406	407	409	411	412	413	415	417
6.		418	419	421	423	424	425	427	429	430	431
7.		433	435	436	437	439	441	442	443	445	447
8.		448	450	451	453	454	456	458	459	461	462
9.		464	465	467	469	470	471	473	475	476	477

Table 4. INDEX OF REFRACTION OF AQUEOUS SOLUTIONS OF SUCROSE
(CANE SUGAR)

The temperature characteristic of the cell is given in Figure 19 in which the index difference between the reference cell held at 20°C, and sample cell at various temperatures is plotted for both deionized water and nominally 1.25 M H₂SiF₆. Note the observed temperature coefficients of the Hydrofluosilicic acid solution and water are essentially identical at $\sim 1.25 \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$. For comparison, the tabulated index temperature coefficient for H₂O in this temperature range is $0.92 \times 10^{-4} \text{ }^{\circ}\text{C}^{-1}$, requiring $\sim +30\%$ instrumental correction factor (probably due to the temperature response of the cell's plexiglass)

⁶Note there are several commercial Abbe type liquid refractometers available at Honeywell, but because of the corrosivity of the etchant, it was decided to construct a specialized apparatus to do these measurements.

⁷Data from The Handbook of Chemistry and Physics, The Chemical Rubber Publishing Company. The data is for 20°C and $\lambda = 5903 \text{ \AA}$. Dispersion is neglected in calibration at the 6328 Å He-Ne laser line.

Figure 18. Differential Index Cell Calibration
Index vs Deflection (H_2O Reference)

Figure 19. Differential Index Cell Temperature Characteristic

for absolute measurements; however, for the remaining measurements, the cell compartments were isothermally thermostated at 25°C, so that this correction was unnecessary.

Using this apparatus, calibrated as described, the index of aqueous Hydrofluosilicic acid was measured as a function of concentration. This data is plotted in Figure 20. Note that commercial Hydrofluosilicic acid is available in aqueous solution ranging in assayed concentrations typically from 25 to 31%. For a 25% concentration reagent, dilution of 2 parts reagent to 1 part H₂O (i.e., 66.7 volume %) gives the 1.25 M nominal etchant recipe concentration; however, as determined by AA and IC analysis, a 66.7% volume solution of this particular batch of reagent was actually 1.295 M. Using these data allows the concentration of the etchant starting H₂SiF₆ solution to be determined within $\pm\frac{1}{2}\%$ via this relatively rapid and straight-forward optical measurement. Thus variations in the lot to lot concentrations of commercially available Hydrofluosilicic acid may be determined and compensated for.

Saturation of this starting Hydrofluosilicic acid solution with excess silica (12 g/l of Baker Chemical Silica Gel 60-200 mesh powder #5-3405) with constant stirring for several hours at 45°C results in 1 to 2 g/l of excess silica gel reacted as determined gravimetrically by filtering to the Whatman 42 level and weighing the ashed filtrate. Comparing several H₂SiF₆ etching solutions (with starting concentrations ranging from 1.20 - 1.30 M), saturated versus unsaturated, gave the initially unexpected result that the saturated solution had a lower index of refraction than the unsaturated solution (by about 1 part in 10⁴); however, once the particulate/colloid nature of the saturated etchant is realized, this result is consistent, in that the physical properties of colloids tend to be more like the dispersing medium than that of the dispersed phase. If the excess silica had truly been solvated in the etchant solution, an increase in index would be expected, just as salt water or the sucrose calibration solutions have higher indices than pure water.

Tracking saturated etchants throughout the etching process with this apparatus gave the following results: working etchants (i.e. doped to the proper potency) have an index only slightly below (1 part in 10⁴) the undoped solutions. Non-working etchants had lower indices with the general trend, the lower the potency,

Figure 20. Calibration-Refractive Index ($\approx 6328 \text{ \AA}$, 25°C) of Aqueous H_2SiF_6 vs Concentration

the lower the measured index. Note that these index differences fell very close to the limit of resolution of this prototype apparatus; it is likely that these small differences are a manifestation of the irreversible aging reactions which deplete the liquid phase of the etchant via silica coagulation and oxyfluoride precipitation as will be discussed in more detail in the process chemical mechanism model.

Coulter Counter

A Coulter counter is an instrument for the determination of particle size distribution which operates by passing a suspension of the particles to be determined diluted in an appropriate electrolyte through an electroded orifice of known dimensions. As indicated in Figure 21, signal pulses are thus generated, the amplitudes of which are directly proportional to the size of the passing particle. Subsequent signal processing using discriminated multichannel scaling, yields both the percent volume of solids and population distributions as a function of particle size.

Figure 21. Coulter Counter

The Coulter counter data presented in the following plots directly demonstrate the particulate/colloid nature of the etchant. Figures 22, 23, 24 and 25 give the percent volume and the percent population size distributions for a series of etchants of 0, -16, -20, and -24 potency (These are the same etchants used to produce the samples of Figures 33, 34, 35). Note for these data, the etchant

%
Volume

%
Population

Figure 22. Etchant Particle Size Distribution
Via Coulter Counter $P = 0$

%
Volume

%
Population

Figure 23. Etchant Particle Size Distribution
Via Coulter Counter P = -16

%
Volume

%
Population

Figure 24. Etchant Particle Size Distribution
Via Coulter Counter P = -20

%
Volume

%
Population

Figure 25. Etchant Particle Size Distribution
Via Coulter Counter P = -24

was diluted 250/1 in normal saline solution and ultrasonically dispersed with wetting agent, with a total of 50,000 particles counted for each distribution determination. A 100 micron diameter orifice was used which was the smallest available for this particular instrument.

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 26 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 27. 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 3. 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 28. 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.

Figure 26. Normalized $\square A$ vs Potency for Series I samples via PIC

Figure 27. $[F]$ vs Potency via IC

Figure 28. 31 vs Potency
via AA

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.

Refractive Index Data

From the calibration curve, Figure 20, the concentration of the etchant starting H_2SiF_6 solution may be determined relatively rapidly with this measurement technique. Variations in the lot to lot concentrations of commercial H_2SiF_6 reagent may thus be monitored and compensated for.

The relative insensitivity of the etchant refractive index to the amount of excess reacted silica gel is interpretable as a manifestation of the colloidal nature of this system.

Coulter Counter Data

Though somewhat noisy, the data of Figures 22, 23, 24, and 25 show that as the potency is lowered, the percent volume distribution mode shifts toward larger particle size, while the percent population distribution shifts to smaller mean size, indicating particle agglomeration to have occurred; this lowers the available SiO_2 surface to volume ratio, and thus its effective chemical activity. Since S/V scales as $1/r$, this phenomenon is much more significant in the submicron particle size regime, which unfortunately is out of the range of size determination of the technique.

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 29, with the "best" fit straight lines, the determined F/Si ratio is very close to 3/1. Listing the possible oxyfluorides⁸ in Table 5, 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 5. Oxyfluoride Stoichiometry

ANALYTICAL TECHNIQUE SUMMARY

The analytical techniques surveyed in the program for application to this problem are summarized in Table 6.

PHENOMENOLOGICAL CHEMICAL PROCESS MODEL

From the data/observations gained in the course of this program the following phenomenological model⁷ of the chemical mechanism of the AR etching process was

$$\frac{[F]}{[S1]} \sim \text{ratio of slopes} \sim 2.95 \quad 43$$

Figure 29. Graphical Average Stoichiometry Determination

Table 6. Analytical Technique Summary

ANALYTICAL TECHNIQUE	INSTRUMENT	DETERMINED PARAMETER	MEASUREMENT TIME WITH SAMPLE PREPARATION	ACCURACY	OBSERVATIONS/COMMENTS
Atomic Absorption AA	Perkin Elmer 603	[Si]	15 Minutes	$\pm 10\%$	Independently determined standards required. Si assumed to be dissolved/complexed totally in liquid phase. Data very noisy due in part to actual particulate/colloid nature of etchant.
High Pressure (Performance) Liquid Chromatography HPLC	Dionex Corp.	[F ⁻]	15 Minutes	$\pm 2\%$	Independently determined standards required. Very sensitive technique requires a large dilution factor (1:10 ⁴) which is the major source of error. Conductimetric detector sensitive only to totally solvated ionized phase.
Ion Chromatography IC					
Paired Ion Chromatography PIC	Waters Associates	[Si, O, F] complex	20 Minutes	$\pm 5\%$	Composition/stoichiometry of separated components not determined. Detectors used only sensitive to liquid phase components. Elution peaks decrease with lower potency.
Infrared Spectroscopy	Beckman 4240 Spectrophotometer	NIR Optical Transmission	15 Minutes	not quantified	Optical transmission decreased with decreasing potency because of scattering from particulate phase formed in the sample cell.
Refractive Index Measurement	Honeywell designed differential cell-laser optical lever technique	[H ₂ SiF ₆]	5 Minutes	$\pm \frac{1}{2}\%$	Independently determined standard required. On reaction with excess silica gel the etchant index is observed to decrease 1 part in 10 ⁴ , indicating a colloidal sol-solvent dispersion, rather than a solute-solvent dissolution to have occurred. The index decreases slightly with decreasing potency.
Coulter Counter	Coulter model T	Particle size distribution by % of solids volume and % population	1 Hour	Depends on sampling technique and Poisson statistics	Direct evidence of the colloidal nature of the etchant. Smallest particle size determinable is ~1 micron; however, the submicron population of particles account for a major portion of the effective interaction active S/V of the sol. Particle agglomeration is observed with decreasing potency.

developed identifying the role of the key reaction species:

The fundamental etchant equilibrium is

1⁹

where reaction with excess $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ drives equilibrium 1 to the right.

Figure 30. Etchant Surface Layer Attack

On immersion on the etchant, HF attacks the glass surface (also via equilibrium 1) to expose a local volume around the alkali sites which subsequently hydrolyzes via:

2

Now H_4SiO_4 polymerizes in situ on the glass surface via siloxane cross-linking

⁹The nominal etchant concentration is 1.25 M H_2SiF_6 (aqueous)

Figure 31. In Situ Gel Formation

This produces a porous gel network which is stable against F^- attack if equilibrium 1 is sufficiently driven to the right.

Differential diffusion through this porous in situ formed gel allows selective removal about the Na sites (thus producing the reduced surface index of refractive antireflection layer) where

4

completes the equilibria involved.

Note these equilibria must operate in definite dynamic range in order to achieve effective antireflection; i.e. if the diffusion rate is:

- 1) "too fast" (gel layer too thin, pore size too large), the glass surface will simply be uniformly attacked.
- 2) "too slow" (gel layer too thick, pore size too small), the glass surface is essentially protected by the gel layer.

This is schematically illustrated in Figures 30, 31 and 32.

Figure 32.¹⁰ Effective Index Versus Distance From Surface

Experimental evidence supporting the formation of an in situ differentially permeable gel layer as a key step in this process is presented in Figures 33, 34, and 35. These are Nomarski photomicrographs of the surface of etched glass samples removed directly from the etching bath without a post etch rinse step and allowed to air-dry. The microstructure of the resulting gel remnant is clearly delineated in these figures. Note as the potency is lowered, the gel layer becomes more dense and less porous, with the pore size characteristic of working etchants falling in the range of 175 to 250 microns. Potency variations of ± 4 units around the operating point produce pore sizes of 400 microns at +4 and 75 microns at -4 respectively.

It is seen that the problem in effectively controlling this process involves a delicate kinetic balancing act between equilibria 1 and 2. Clearly for a given temperature and H_2SiF_6 concentration, the amount of silica reacted with the etchant is the primary control parameter; however, as borne out by the experimental evidence to date, the particulate/colloid nature of this system (i.e. the etchant does not exist in a simple single liquid phase) complicates matters so that the total amount of reacted silica is not uniquely defined by a single concentration value. The effective surface to volume (S/V) ratio of the

¹⁰ Previous microstructural studies of the AR layer produced by this process show a skeletonized structure with pore sizes a few hundred angstroms across. Optically this skeletonized layer behaves almost identically to the classic quarter wave MgF_2 antireflection coating, acting as a homogeneous intermediate index coupling layer as has been schematically illustrated in this figure.

64X

640 X

→|← ~ 190 microns

Figure 33. Gel Remnant Microstructure
Potency -20, P ~ P
optimum

64 X

640 X ~ 390 microns

Figure 34. Gel Remnant Microstructure
Potency -16, $P > P_{\text{optimum}}$

64 X

640 X

~ 75 microns

Figure 35. Gel Remnant Microstructure
Potency -24, $P < P_{\text{optimum}}$

available silica also has a critical role in determining the system's kinetic operating point. That is, the higher/lower S/V, the more equilibrium 1 is driven to the right/left for a given amount of HF; this in turn depends on the specific details of the etchant solution preparation/mixing technique and filtration level.

The effect of the potency doping reagents is to adjust the equilibrium point of 1

where:

- i) adding F^- (increasing the potency) shifts 1 to the right, and
- ii) adding B(OH)_3 , Boric acid (decreasing the potency) shifts 1 to the left via

which ties up F^- in a lower activity complex BF_4^- . (The BF_4^- anion has a lower chemical activity because of its larger size compared to F^- .)

There also appears to be a synergistic effect involved, since as equilibrium 1 is driven to the left, the SiO_2 tends to agglomerate, thus lowering its S/V, farther driving 1 to the left.

As discussed previously, this leads to the formation of an oxyfluoride precipitate via the competing reaction

which acts as a primary aging mechanism of the etchant. Notice as aging reaction 6 proceeds, twice as much SiO_2 is consumed as required in equilibrium 1, leading to an "excess" of HF which eventually shifts the equilibrium point of 1 to the right; thus, as the etchant bath ages, farther negative potency dopings (Boric acid additions) are required to maintain the operating point.

PROCESS CONTROL/METHODS

The problem of glass etching process control is schematicized in the flow chart diagram of Figure 36 in which the notation

is used.

As indicated in the flow chart, Figure 36, the process is logically divided into four steps: 1) hydrofluosilicic acid reagent dilution to starting concentration, 2) reaction/saturation with excess silica gel, 3) potency adjustments, and 4) panel immersion/etching. Of these steps, the second and third are the most difficult to monitor and control.

Figure 37 schematicizes an abridged process control scheme which has proven useful in laboratory scale etching batches. As diagrammed, the initial hydrofluosilicic acid concentration is determined by index of refraction measurements. It was found through approximately 20 laboratory scale etchant batch preparations done over a period of three months, that if the initial acid concentrations were controlled, and the mixing parameters kept reasonably fixed, the etchants operated consistently in the -16 to -20 potency range. Using paired ion chromatography (PIC) with a modified sampling/sample preparation technique to take into account the particulate nature of the etchant

Process Step 1: M_2SiF_6 dilution to starting concentration

Process Step 2: Reaction/Saturation with excess Silica gel

Process Step 3: Potency Adjustments

Process Step 4: Etching

Figure 36. Process Control Flow Chart

Figure 37. Abridged Process Control Scheme

(sample dilution followed by filtration to the 0.45 micron level rather than 2 micron level filtration followed by dilution as was used for the data of previous samples presented in Figure 26), the etchant concentration (component A) may be tracked as shown in Figure 38. Alternatively the gel remnant microstructure of test samples may be examined for pore spacing (as in Figures 33, 34, 35) to determine the etchant operating point for in-process adjustments as required.

CONCLUSIONS AND RECOMMENDATIONS

The main result of this work is the experimental evidence indicating that the etchant does not operate in a simple single liquid phase, but that its particulate/colloid properties play an important role in determining the process equilibrium operating point. This complicates the problem of process monitor/control, but a scheme has been devised which has proven adequate at least in laboratory scale etching. Minor modifications including refinements of sampling/sample preparation techniques must be accomplished before application of these techniques to a full scale AR etching process production line. This will be investigated during the add-on phase of this contract in which the etch AR coating large-scale production process is to be extended to new types of glass not previously used, but which are now expected to dominate the solar collector cover market.

Figure 38. Normalized [A] Vs. Potency
Modified Sample Preparation Technique

SECTION III

ORGANIC AR COATINGS

INTRODUCTION

Work in a previous program (Reference 1) demonstrated the feasibility of fused Teflon FEP-120 as a cost effective antireflection (AR) coating for flat plate solar collector glass glazing applications. The Teflon FEP-120 fluorocarbon coating material is a water based dispersion of hexafluoropropylene-tetrafluoroethylene copolymer particles having a refractive index of $n_D \approx 1.34$. Although not as optically efficient, this material used as a coating on glass promises advantages over etched glass with respect to soil release, lower cost and better long term outdoor durability. Work in the current program shows promise of improving the transmittance of glass by 4.7% at less than 1¢/ft² for material cost. This development effort emphasized handling durability, abrasion resistance, solution stability, optical efficiency, thickness control, simulated exterior exposure, cost, and scale-up.

COATING TECHNIQUES

Various coating techniques for applying the organic teflon dispersion to solar collector glass cover plates were assessed. Because good optical performance requires tight coating thickness control, several techniques such as spray coating may be ruled out immediately. Other methods of coating offering precise thickness control, such as spin coating, were considered impractical because of the large size of the glass glazings involved. Therefore dip coating technique development was emphasized in this program as the simplest approach offering good thickness control and relatively straight-forward process scale-up.

Promising results were achieved by using dip coating techniques with Teflon FEP-120 on glass as shown in Figure 39. An increase in solar transmittance

Figure 39. Solar Transmittance Increase of Glass,
Dip Coated at Various Rates in 8%
Solids FEP-120 Teflon Dispersion

of 4.7% was achieved with a coating solution of 8% solids and a dip rate of 2.0 in./min. Thickness control was maintained by this technique to provide low reflectance. The thickness of this coating was estimated to be ~ 0.01 mil. ($0.25 \mu\text{m}$). The estimated material cost for Teflon FEP-120 coatings of this thickness applied to glass is 0.20¢/ft^2 for both surfaces.

Thickness Optimization

Dip coating rate and coating solids content determine the AR layer thickness. These parameters were systematically varied to optimize the coating thickness and thus the transmittance of the coated glass.

The Teflon FEP-120 dispersion was received from Dupont at $\sim 55\%$ solids and diluted to 8% with deionized 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 $0.35 - 0.75 \mu\text{m}$ using a Beckman DBG spectrophotometer or Beckman DK-2A Spectrophotometer, with integrating sphere attachments to provide total transmittance.

Cleaned glass substrates were coated with the 8% solids Teflon FEP-120 dispersion at dip coating rates of 2 - 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 slowly cooling to room temperature, the transmittance of the 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 as shown in Figure 39. Note that the transmittance increase was greater at slower dip rates (i.e., 2 - 4 in./min.) than at faster dip rates (i.e., 6 - 20 in./min.). It is evident that dip rates of 2 - 4 in./min. offer the highest increase in transmittance (4.7%).

Another set of experiments was conducted to provide data on the effect of coating solids concentration on transmittance increase. The Teflon FEP-120 dispersion was diluted to 2 - 30 percent solids with deionized water. Coatings were made on glass substrates at 2 in./min. and 4 in./min. dip coating rates, fused, and measured as before. The increase in solar transmittance was plotted as a function of coating solids concentration in Figures 40 and 41.

Figures 40 and 41 illustrate the satisfactory correlation of the transmittance characteristics of samples run during the previous feasibility study (Reference 1) and samples prepared recently. A new dip coater allowed more precise control of the dipping parameters in the processing of the current samples. This improvement resulted 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 optimum range of dispersion solids concentration is from 4 to 12 percent. Transmittance increases of as much as 4.7 - 4.9 percent were achieved using the optimally diluted Teflon FEP-120 dispersion and a 2 in./min. dip rate.

SOLUTION STABILITY

During the early part of this development effort, it became apparent that there were significant lot-to-lot variations in the Teflon FEP-120 dispersions and that these variations adversely affected the optical efficiency, adhesion and abrasion resistance of the coating. As a result of this problem, new material was ordered each month to maintain a fresh stock and old material was periodically evaluated for coating process effectiveness. The origin of this aging/degradation phenomenon is not immediately obvious, but it appears to occur either in the manufacture, shipment, and/or storage of the material. The solution aging study results are shown in the transmittance data of Table 7, while Figure 42 is a plot of optical performance vs solution age for coatings produced from three different lots of Teflon FEP-120 dispersion (diluted to 8% solids).

From Table 7, it can be seen that lot 762 provides increased transmittance of 4.7% when evaluated four weeks after receipt from the vendor (Dupont). One

Figure 40. Solar Transmittance Increase Of
Glass Dip Coated at 2 in/min

Figure 41. Solar Transmittance Increase Of
Glass Dip Coated at 4 in/min

Table 7. Teflon FEP-120 Solution
Aging Study Data

Lot Number	Weeks After Receipt	Transmittance Increase (%)
762	4	4.7
	5	4.2
	17	3.1
	28	3.1
	32	3.5
	34	4.2
	38	3.7
791 "A"	4	4.9
	6	3.9
	7	4.1
	14	3.8
	19	3.7
	24	4.2
791 "B"	4	3.5
	8	3.5
	13	4.2
	17	4.2

Figure 42. Coating Optical Performance vs Solution Age

week later this same lot of coating dispersion provided 4.2% increased transmittance, a drop of 0.5%. Seventeen weeks after receipt, the same lot of material provided a 3.1% increase in transmittance, a drop of 1.6% from that of the coating made four weeks after receipt. The test was repeated to 38 weeks with varying transmittance fluctuations, as indicated in Figure 42.

Lot 791 "B", which was ordered after lot 791 "A", was evaluated four weeks after receipt and showed a transmittance increase of 3.5%. (The "A" and "B" designations were arbitrarily assigned to distinguish between two shipments of the same lot of Teflon FEP-120 dispersion).

Note the vendor recommends periodic agitation of the dispersion on a weekly basis to maintain its particle suspension. Although there was no scheduled agitation for the lots, the dispersions were agitated prior to each use. As the data in Table 7 and Figure 42 show, this agitation failed to alter the degradation of the dispersion for AR coating purposes.

Presumably lot 791 "B" was properly agitated by the vendor prior to shipment, yet it produced coatings with significantly lower transmittance increase than the same lot of material shipped earlier. The results from lot 791 "B" are shown in Table 7. Although the data is somewhat incomplete, it suggests that the lower limit of the transmittance increase produced by a coating of aged material is about 3.5%. With 3.5% increased transmittance, the FEP-120 dispersion at an estimated material cost of less than $1¢/ft^2$ still remains a viable low cost AR coating.

The stability of the AR Teflon coating solution was also evaluated after being diluted from 55% solids to 8% solids with water. Once diluted, the material tends to coagulate and fall from suspension to the bottom of the container. Samples were processed daily (using a dip rate of 2 in./min.) up to 7 days after the original dilution and their transmittance measured. This data is presented in Figure 43. It can be seen that the coating solution is fairly stable to 4 days of aging with 4.9% transmittance increase, and then

Figure 43. Coating Optical Performance Vs.
8% Solids Teflon FEP-120 Process
Solution Age After Dilution

begins to degrade consistently. The 4 day stability of the coating solution would be compatible with production application. An agitation system could be employed to aid in maintaining particle suspension to increase solution stability.

COATING DURABILITY

Our initial work with the FEP-120 fluorocarbon dispersion applied directly to glass resulted in coatings easily damaged by handling. Handling at the factory, during installation in the collector, or in mounting the collector on site could damage the AR coating. The problem was related to both adhesion of the coating to the glass and to the abrasion resistance of the coating. It was believed that if the adhesion of the AR coating could be improved, durability would improve. Since little can be done to improve the intrinsic abrasion resistance of the coating short of modifying the polymer through long range synthetic chemical development, emphasis was placed on improvements in adhesion. Glass etch pretreatments with hydrofluoric acid (HF) and adhesion promoters were explored in an attempt to improve adhesion.

Hydrofluoric Acid Etching

Initial development concentrated on increasing the surface area and removing the weathered surface layer from the glass through etching in hydrofluoric (HF) acid solutions. Hydrofluoric acid concentrations from 0.01 to 5 percent and etch times (at room temperature) from 30 seconds to 5 minutes were used. The etched substrates were coated with an 8 percent solids Teflon FEP-120 dispersion at 2 in./min. and fused at $775 \pm 10^{\circ}\text{F}$ for 10 - 15 minutes. Transmittance measurements were taken before and after exposure to abrasion. The abrasion test consisted of rubbing the coated glass with cheesecloth under 0.7 psi for 100 cycles (200 strokes). The results are shown in Table 8.

Table 8 does not show any definite pattern or trend. The only information from Table 8, which indicates a somewhat inconsistent pattern, was that some samples etched more deeply (i.e., longer time at low concentration or short time at

Table 8. Solar Hemispherical Transmittance
of Organic AR Coated Glass, Before
and After Abrasion Testing

Etching Condition		Solar Transmittance (%)		
HF Conc., (%)	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
0.01	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

Notes:

- 1) Coating Parameters: 8% solids, coated at 2 in/min.
- 2) Abrasion Test: Gardner Straight Line Washability and Abrasion Machine

higher concentrations) had an increase in transmittance after the abrasion test. Because of the lack of a specific pattern from the data in Table 8, a second test was conducted to better define the effect of etching the glass on the abrasion resistance of the Teflon FEP-120 coating. Hydrofluoric acid concentrations were varied from 0.01 to 5 percent and glass immersion times from 0.5 to 5 minutes. Teflon FEP-120 dispersion at 10 percent solids was dip applied at 2 in./min. to glass substrates, air dried and fused as before. Transmittance was measured before and after abrasion exposure as shown in Table 9.

From Table 9, it appears that as the etching time on hydrofluoric acid concentration 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 appears to have increased after exposure to abrasion, which may be an instrumental artifact. (The instrumental resolution is $\pm 0.2\%$ in transmittance and the observed increases are within this margin of error.)

Table 10 shows the solar transmittance results before and after 100 cycles of 0.7 psi abrasion testing of 8% Solids Teflon FEP-120 coated glass substrates dipped at 2 in./min. Prior to coating, the glass substrates were etched with 0.10% hydrofluoric acid concentration at exposure times ranging from 0 to 10 minutes. The data in Table 10 is the average transmittance of four different substrates to achieve a more accurate measurement. A definite pattern exists, which indicates an improvement in abrasion resistance with respect to exposure time of the acid. An exposure time of 0.25 minutes resulted in a transmittance loss due to abrasion of 1.5%. It was evident that abrasion resistance was improved linearly with increased etch exposure time, up to 5 minutes of acid exposure with only 0.1% transmittance loss after abrasion testing; abrasion resistance decreases after 7 minutes of exposure to a 0.3% transmittance loss.

Silane Coupling Agent Adhesion Promotor

The adhesion of the Teflon FEP-120 coating was improved dramatically by using an amino-functional silane (Z-6020) adhesion promotor from Dow Corning. The

Table 9. Solar Hemispherical Transmittance
of Organic AR Coated Glass Before
and After Abrasion Testing²

Etching Condition		Solar Transmittance (%)		
HF Conc (%)	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

Notes

- 1) Coating Parameters: 10% solids, coated at 2 in./min.
- 2) Abrasion Test: Gardner Straight Line Washability and Abrasion Machine

Table 10. Solar Hemispherical Transmittance
of Organic AR Coated Glass, Before
and After Abrasion Testing²

Etching Conditions		Solar Transmittance (%)		
HF Conc (%)	Time (Min)	Before	After	Difference
0	0	95.3	94.3	1.0
0.10	0.25	95.3	93.8	1.5
0.10	0.50	95.3	94.4	0.9
0.10	1.0	95.3	94.5	0.8
0.10	3.0	95.0	94.5	0.5
0.10	5.0	94.9	94.8	0.1
0.10	7.0	94.7	94.4	0.3
0.10	10.0	94.9	94.4	0.5

Notes:

- 1) Coating Parameters: 8% solids, coated at 2 in./min.
- 2) Abrasion Test: Gardner Straight Line Washability and Abrasion Machine
- 3) Transmission Data: Average of 4 samples for each etching series

silane acts as a coupling agent between the organic Teflon coating and the inorganic glass substrate. This particular silane agent was chosen because of its double organic bonding reaction sites. The procedure for using the adhesion promoter involved soaking the glass substrate in a 0.5% solution of silane for 1 - 5 minutes. After the silane promoter was completely dry, the Teflon FEP-120 coating was applied using the usual dipping technique at 2 inches/minute and fused. However, since there was some concern that during the usual fusion cycle (775°F for 15 minutes) the silane coupling agent might degrade, a lower temperature fusion cycle was used (550°F for 15 minutes).

Upon completing the usual abrasion test, it was found that significant improvement was achieved by using the adhesion promoter as determined by percent coating loss measurements. The samples were also exposed to accelerated weathering and humidity-temperature testing along with control samples without the adhesion promoter treatment. The results are shown in Tables 11 and 12. It is evident from Table 11 that the weathering durability increases significantly with the silane treatment. For example, after 170 hours of accelerated weathering, 75% of the AR coating is lost from untreated substrates, while only 2% of the coating is lost from silane treated samples. Table 12 shows similar results (though not quite as dramatic) after temperature/humidity testing.

Weathering/Humidity Tests

Simulated/accelerated weathering and humidity cycle testing present a severe test for the durability of these organic AR coatings. In this section, the results of such testing are presented.

The accelerated weathering test of FTMS 141A Method 6152 was conducted using an Atlas Twin Arc Weather-O-Meter, model XVDL. (In this chamber, ~500 hours is equivalent to three years outdoor exposure). The humidity cycle test of MIL-STD-810B was conducted in a Webber Engineering Corporation Chamber. Samples were prepared with an HF etch step (0.1% HF) with varying etch times and processed as usual with a 2 in./min. dip in an 8% solids FEP-120 solution and fused.

Table 11. Loss of Organic AR Coating After Accelerated Weathering Testing¹

Exposure	PERCENT COATING LOSS ²				
	Without Silane Treatment	With Silane Treatment			
		1 min	2 min	3 min	5 min
40	0	0	0	0	0
50	4	0	0	0	0
100	19	1	1	1	1
125	41	1	1	1	1
170	75	2	2	2	2
210	-	2	2	2	2
340	-	5	5	5	5

Notes

- 1) Weathering Test: Atlas Twin Arc Weather-O-Meter, Model XVCL, accordance with Federal Test Method Standard 141, Method 6152.
- 2) Loss Determination: Percent coating loss based on visual observations

Table 12. Loss of Organic AR Coating
After Temperature/Humidity Testing

PERCENT COATING LOSS					
Exposure	Without Silane Treatment	With Silane Treatment			
		1 min	2 min	3 min	5 min
50	1	0	0	0	0
100	1	0	0	0	0
240	6	2	2	2	2
340	-	2	2	2	2
410	-	4	4	5	4

Notes

- 1) Temperature/Humidity Test: Humidity Chamber, Webber Engineering Corp., according to MIL-STD-810B.
- 2) Loss Determination: Percent coating loss based on visual observations.

Table 13 shows the change in coating optical performance after 86 hours of accelerated weathering, while Table 14 gives the results after 168 hours of humidity exposure. Note from these data that samples that were etched 5 minutes or longer exhibited very poor weathering durability, in contrast to the results of Table 10 which indicated an optimization of mechanical abrasion resistance at these process etch parameters. On the theory that the poor durability of etch treated glass to accelerated weathering and humidity cycling might be due to residual HF reactivation during these tests, a 20% NH_4OH neutralization step was added to the etch processing. No improvements were gained by adding this step.

COATING PROCESS IMPROVEMENT STUDY

In this section the results of refinements/variations on the basic coating processing technique are discussed.

Vapor Phase

In the current dip coating procedure, the glass substrates are withdrawn after total immersion in a half-filled container of FEP-120 solution of 2.0 in./min. To investigate the possibility that volatile solvents from the Teflon material were deleteriously interacting with the just coated substrate in the dead-zone above the liquid level in the dip reservoir, steps were taken to eliminate this vapor phase by the simple expedient of filling the reservoir all the way to the top. This processing step modification brought no significant coating durability improvement, leading to the conclusion that the vapor phase plays no significant role here.

Particle Size

The effect of particle size in the Teflon dispersion on coating optical performance and durability was assessed. Using centrifugal sedimentation techniques, the dispersion particles were roughly separated into large and

Table 13. Coating Loss and Transmittance Change After 86 Hours of Accelerated Weathering Testing

Etching Conditions		Solar Transmittance			Percent
HF Conc (%)	Time (Min)	Before	After	Difference	Coating Loss
0.1	0.5	94.6	94.2	0.4	1
0.1	1.0	94.3	93.9	0.4	1
0.1	3.0	94.5	94.4	0.1	15
0.1	5.0	94.9	90.4	4.5	100
0.1	7.0	94.5	90.1	4.4	100
0.1	10.0	94.3	89.8	4.5	100

Table 14. Coating Loss and Transmittance Change After 168 Hours
MIL-STD-810B Humidity Testing

Etching Conditions		Solar Transmittance			Percent ²
HF Conc (%)	Time (Min)	Before	After	Difference	Coating Loss
0.1	1.0	94.7	93.1	1.6	30%
0.1	3.0	94.5	92.9	1.6	5%
0.1	5.0	95.3	92.1	3.2	50%
0.1	7.0	94.5	92.5	2.0	30%
0.1	10.0	94.8	92.6	2.2	40%

small sized particle groupings (the dividing line between the two groups was arbitrary) and coatings were formulated in the usual manner from each of the two groups. No significant difference was found between the two coating classes with respect to durability or AR effect so that either particle size is irrelevant to coating performance, or all the particles in the dispersion are uniform. To elucidate this farther, a sample suitable for scanning electron microscope (SEM) analysis was prepared from a dilute (2% solids) solution of FEP-120. The scan (5000X) is shown in Figure 44. Note all the individual particles are relatively uniform in size (0.2 - 0.3 microns in diameter) with some degree of agglomeration and clustering evident.

Fusion Cycle

The fusion cycle required for converting Teflon FEP-120 material into a useable coating occurs in three steps: 1) removal of water at room ambient and elevated temperature, 2) removal of wetting agent, and 3) fusion of particles to form a film.

In choosing a fusion cycle, two considerations must be balanced. The time should be long enough and the temperature high enough to achieve adequate melting and flow, but not so long or so high that significant decomposition of the resin occurs.

Resistance of the Teflon AR coating on glass to accelerated weathering and humidity exposure was found to be related directly to the fusing schedule. Originally, coatings were fused at $775 \pm 10^{\circ}\text{F}$ for 10 - 15 minutes. This was believed to be too high, where significant decomposition of the resin and carbonization of the wetting agent could occur and cause poor durability. The wetting agent (Triton X-100) which is used to maintain a suspension of the Teflon FEP-120 dispersion, readily volatilizes at 500°F . At temperatures in the region of 700°F the wetting agent may carbonize and form residues in the coating. Therefore, the temperature range studied was between $550 - 700^{\circ}\text{F}$.

Samples were prepared in the usual manner, and fused at $550 - 775^{\circ}\text{F}$ for 1 - 4 minutes and the increase in solar transmittance measured.

2% SOLIDS (NOT FUSED)

5000 X

| | = 1 micron

FIGURE 44. Particles of Teflon FEP-120 Antireflection Coating Material

As can be seen from Figure 45, the best optical performance occurs for a fusion cycle of 1 minute at 625°F. (Note that the transmittance increases for this series of samples are lower than normal because of previously discussed solution aging effects, but the results are still valid for comparison purposes.)

Tables 15 and 16 show the total percent loss at various fusing temperatures and times after 218 hours of accelerated weathering and 336 hours of humidity exposure respectively. It is evident from this data, that the previous fusing temperature of 775 ± 10°F for 10 - 15 minutes was too high, with 100% coating loss after 218 hours of accelerated weathering and 50% after 336 hours of humidity exposure. It was previously noted that a fusing schedule of 625°F for 1 minute produced the best AR coating performance; however, as shown in Tables 15 and 16, this fusion cycle gives unacceptably high (~50%) coating losses upon weathering and humidity exposure.

It can be seen from Tables 15 and 16 that fusing temperatures of 700 and 550°F with respect to low exposure times offer optimum durability. A fusing schedule of 700°F for 1 minute resulted in no visual coating loss from accelerated weathering and only 5% after humidity exposure.

To confirm the optimization of coating durability at these fusion cycles, further tests were performed on various 2" x 3" glass substrates. The substrates used for the test were: 1) plain glass as a control, 2) 0.1% hydrofluoric acid etched, 3) 0.5% silane coupling agent treated, and 4) combined etched and silane treated. These test panels were coated and fused at 500°F for 15 minutes and 700°F for 1 minute which were found to offer the most durable coating in the previous tests. Panels were measured for increase in transmittance and then exposed to 480 hours of accelerated weathering and 720 hours of humidity environment. The results are given in Table 17.

From these data it is clear that the coatings are the most stable with the 700°F - 1 minute fusion cycle processing. Note that single stage etch pre-treated samples show poor durability performance with 95% coating loss after

1

TABLE 15. COATING LOSS AFTER WEATHERING TESTING
(218 HOURS) FOR VARIOUS FUSION CYCLES

TEMP. °F	TIME, MINUTES				
	1	5	15	30	45
775 ± 10	20%	98%	100%	100%	ND ²
700 ± 10	0%	75%	99%	50%	ND
625 ± 10	50%	40%	70%	99%	90%
550 ± 10	ND	15%	10%	0%	30%

1

TABLE 16. COATING LOSS AFTER HUMIDITY TESTING
(336 HOURS OF 810B) FOR VARIOUS
FUSION CYCLES

TEMP. °F	TIME, MINUTES				
	1	5	15	30	45
775 ± 10	10%	20%	50%	100%	ND ²
700 ± 10	5%	10%	15%	5%	ND
625 ± 10	50%	60%	30%	30%	40%
550 ± 10	ND	20%	40%	15%	25%

1) Percent loss based on visual observations.

2) ND = No Data.

Table 17 TRANSMITTANCE AND COATING LOSS AFTER ACCELERATED WEATHERING AND HUMIDITY EXPOSURE OF VARIOUS GLASS SUBSTRATE PREPARATIONS

Fusing Schedule	Glass Substrate	Before Increase %, Trans	480 hrs Weathering ¹		720 hrs Humidity ²	
			Coating ³ Loss	%, Trans. Loss	Coating Loss	%, Trans. Loss
550°F 15 Min.	Plain Glass	4.4	30	2.1	15	2.1
	Etched	4.0	90	3.1	25	2.3
	Silane	4.0	5	1.8	1	1.2
	Etched & Silane	4.3	25	1.1	1	1.5
700°F 1 min.	Plain Glass	3.7	5	0.4	15	1.5
	Etched	4.4	95	1.9	20	1.9
	Silane	4.2	5	1.2	1	0.2
	Etched & Silane	4.1	5	0.7	1	0.7

1) Atlas Twin Arc Weather-O-Meter; Model XVDL, accordance with Federal Test Method Standard 141, Method 6152.

2) Humidity Chamber, Webber Engineering Corp., MIL-STD-810B.

3) Percent coating loss based on visual observation.

accelerated weathering and 20% loss after humidity exposure, but with an additional silane coupling agent processing step, durability is significantly improved, along with maximum retention of the desired AR properties.

Stability of Adhesion Promotor

A study was performed on the stability of the silane adhesion promoter (coupling agent) after dilution to 0.5% with water. The silane solution was left standing for 7 days. Glass substrates were then treated with the silane solution, processed in the usual manner, and then exposed to abrasion testing. (100 strokes at 0.7 psi). Comparing the abrasion durability of samples prepared with aged coupling agent (~7% loss) with that of samples prepared from freshly prepared solution (~3% loss), it is concluded that the solution is fairly stable after dilution and therefore can be used for many days. Solution stability is essential for commercial application.

PRELIMINARY SCALE-UP

Five square feet of glass consisting of five 1 x 1 foot panels were coated to determine process scale-up feasibility. This was an important test since many parameters could be affected which could alter the optimization of the AR coating. Due to the larger thermal loading of the 1 x 1 foot panels compared to the 2 x 3 inch experimental silane treated glass panels, various fusing times (1 - 30 minutes) and temperatures (550 and 700°F) were reevaluated. The best fusing schedule with respect to abrasion durability (0.7 psi, 200 cycles) was 700°F for 5 minutes, as shown in Table 18; however, notice the coating loss was considerably higher than previous results (Table 10). The difference in processing for this series of samples from that of previous work was that the glass panels were treated with silane one day and then Teflon coated the next day, which may have caused poor coating adhesion by allowing the coupling agent time to react with possible atmospheric contaminants. Therefore, it was decided that in the final scale-up demonstration, all the processing should be completed within the same day.

1

Table 18. Abrasion Test Result of Preliminary Process Scale-Up

	FUSING SCHEDULE				
	1 Min. @ 700°F	5 Min. @ 700°F	5 Min. @ 550°F	15 Min @ 550°F	30 Min. @ 555°F
Percent ² Coating Loss	45%	35%	40%	40%	45%

- 1) Gardner Straight Line Washability and Abrasion Machine.
- 2) Percent AR Coating Loss Based on Visual Observations.

FINAL SCALE-UP

The final scale-up consisted of coating 18 square feet of glass. Glass sheets 1 x 1 foot were cleaned by the chromic acid procedure, treated with 0.5% silane adhesion promoter by soaking (exposure) for 3 minutes. The glass sheets were coated with 8% Teflon FEP-120 material then fused at 700°F for 5 minutes. This entire process was done in the same day. Table 19 summarizes the results for 3 representative samples. As indicated in the table, transmittance measurements taken at 4 spots near the edge of each panel show the coating uniformity to be quite good. Also notice, even though the processing was completed within one day, the abrasion durability test results are about the same as for the preliminary scale-up.

Final coatings were exposed to 468 hours of accelerated weathering and 696 hours of humidity testing. The coatings exposed to accelerated weathering lost 15 - 30% of the Teflon FEP-120 coating, while humidity exposure results showed a loss of only 2% of the coating material.

CONCLUSIONS/RECOMMENDATIONS

A low-cost organic AR coating for glass with promising durability has been successfully developed. The coating makes use of commercially available fluorinated ethylene propylene (Teflon FEP-120) solution. It increases the transmission of glass by 4.7 percent (0.35 μm to 0.75 μm) at an estimated material cost of about 0.20¢/ft². Although significant progress has been made to date in the development, a number of problems remain to be solved before the coating becomes a commercial reality. These current limitations of the coating and process are believed to be solvable through additional development.

Table 19. PHYSICAL TESTING RESULTS OF FINAL SCALE-UP OF
TEFLON AR COATED GLASS

Sheet Number	Side ¹	Solar Transmittance, (%)	Abrasion Test ² (%)	Percent Coating Loss ⁵	
				Acc. Weath. ³ (468 Hours)	Humidity ⁴ (696 Hours)
3	T	96.0	40	20	2
	L	95.7	40		
	R	95.9	40		
	B	95.9	40		
10	T	95.8	35	30	2
	L	95.8	35		
	R	94.5	40		
	B	95.9	40		
16	T	95.9	40	15	2
	L	95.4	35		
	R	95.7	40		
	B	96.0	35		

- 1) T=Top, R=Right, L=Left, B=Bottom
- 2) Gardner Straight Line Washability and Abrasion Machine. Percent coating loss based on visual observation.
- 3) Atlas Twin Arc Weather-O-Meter, Model XVDL, accordance with Federal Test Method Standard 141, Method 6152.
- 4) Humidity Chamber, Webber Engineering Corp., according to MIL-STD-810 B.
- 5) Percent Coating Loss Based on Visual Observations

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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 fluosilicic 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 supersaturated 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)