TIME and TEMPERATURE STABILITY of SILVER-COATED CERAMICS for HYDROGEN MASER RESONANT CAVITIES

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ABSTRACT

We have investigated the dimensional stability, as a function of time and temperature, of silver-coated glass-ceramics typical of those used in hydrogen maser resonant cavities. The measurements show that (a) the stress in the silver coating decreases with time at a rate proportional to the initial coating stress, and (b) the variation in stress with temperature is proportional to the initial stress, and decreases with time. Observations indicate that the coating stress can be relieved by precooling the materials.

INTRODUCTION

Like many precision oscillators, the hydrogen maser is subject to long-term ($>10^5$ seconds) frequency drifts, generally assumed to be caused by systematic effects. Masers built by the Smithsonian Astrophysical Observatory (SAO) have been observed to drift toward higher frequencies beginning when they are built, the rate of drift decreasing over periods of months to years. This behavior is believed to be due to a monotonic increase in the resonance frequency of the maser's microwave cavity, which produces a proportional variation in the maser's output frequency through the cavity pulling effect[1]. The cavity frequency drifts are most likely caused by decrease in the cavity's size. (Cavity frequency variations can also be caused by other effects, such as changes in the impedance or reflectivity of external circuits coupled to the cavity.) The resonant cavity consists of a cylindrical tube approximately 24 cm long and 28 cm in diameter, capped by two circular endplates. It is made of a low-expansion glass-ceramic material (Cervit C-101) coated on its inside with silver to form the conductive surface.

A substantial contribution toward the change in cavity size has been identified as shrinkage of the joints between the cavity's cylinder and endplates. Similar shrinkage has been observed in polished, optically contacted joints by Jacobs[2], who found that the length decreased roughly exponentially with a characteristic time on the order of months. Changing the cavity construction from ground to polished joint surfaces has reduced initial frequency drifts substantially. Nevertheless, drift rates on the order of a part in 10^{15} per day remain over periods of years, when joint shrinkage is expected to have become negligible.

Another possible source of cavity frequency drift is change in cavity shape due to relaxation of the mechanical stress in the silver coating. We knew that the coating is under tensile stress at room temperature, bending the endplates concave toward the inside of the cavity. The tensile stress results from the technique by which the silver is applied. The silver coating material is sprayed onto the cavity surface and dried, after which the cavity is fired at 700°C and returned to room temperature over several hours. Oxides in the coating material bond the silver to the substrate at high temperature. As the temperature decreases the silver contracts, resulting in the concave endplate shape. Any decrease in the coating stress would tend to flatten the endplates, shortening the cavity and raising its frequency.

To test this hypothesis we investigated the dimensional stability of silver-coated samples of low-expansion ceramics over a period of six years. Early measurements[3] yielded information on the initial thermal expansivity of the coated samples and on the surface stress produced by grinding the ceramic materials. Here we report on the results of the long-term observations.

EXPERIMENTAL TECHNIQUE

Samples of Cervit C-101 (Owens-Illinois Corp.), Zerodur (Schott Glass Corp.) and ULE (Corning Glass Works) were ground to rectangular shapes, 4x.75x.25 inches (10.2x1.9x0.6 cm). Both broad faces of each sample were polished flat, with enough material removed to eliminate the surface stress caused by grinding. One face was then reground to produce the surface texture found in maser cavities. This face was etched with hydrofluoric acid to remove the grinding stress, as is done with maser cavities, and then coated with silver (Engelhard type 421), using the spraying and heat treatment procedure described above for maser cavities.

The stress in the finished silver coatings was determined from interferometric measurements of the bending of the rectangular samples. Optical interference patterns between the samples and a reference optical flat were created using a He-Ne laser interferometer[4]. The fringe patterns were photographed, manually digitized, and analyzed by a computer program[5] that fits a series of Zernike polynomials to the pattern. A three-parameter fit was used, producing coefficients C_1, C_2 and C_3. C_1 and C_2 are proportional to the tilt of the sample, in two dimensions, relative to the reference flat, while C_3 is proportional to the sample's curvature, often referred to as "focus" in optics. As discussed below, the curvature is proportional to the surface stress in the coating.

To determine the time variation of the coating stress, the effect of temperature must be removed. The curvature was measured at several temperatures during each experiment period. The 1981-82 measurements were made at 23°C and 33°C, with the temperature measured by a mercury thermometer (resolution <0.5°C). The 1988 measurements were carried out at several temperatures between 23°C and 51°C, with the temperature measured by a platinum resistance thermometer (precision <0.1°C) and verified with a thermistor . Between the measurement periods the samples were held at normal room temperature (roughly 23°C) .

RELATIONSHIP BETWEEN SAMPLE BENDING AND COATING STRESS

It can be shown[6] that a thin rectangular beam coated on one side with a stressed film will bend into a parabolic shape. The deflection y a distance x from the center of the beam, with x measured along the beam's long axis, is given by

$$y = \left[\sigma \frac{3(1-\nu)}{E_s} \frac{t_f}{t_s^2}\right] x^2 \tag{1}$$

Here t_s is the beam thickness, ν is the Poisson's ratio of the substrate material, E_s is the substrate's Young's modulus, and t_f and σ are the thickness and internal stress of the film, respectively. The criterion for a "thin" beam is that its length-to-thickness ratio L/t_s should be large compared to unity. For our samples, $L/t_s = 16$, and this criterion is reasonably well satisfied. As shown in the Appendix, a linear relationship exists between the measured Zernike coefficient C_3 and the coating stress:

$$\sigma = \frac{2C_3}{t_f} \frac{E_s}{3(1-\nu)} \left(\frac{t_s}{r_o}\right)^2 \tag{2}$$

For our samples $t_s = 0.635$ cm and $r_o = 5.088$ cm, giving $(t_s/r_o)^2 = 1.51 \times 10^{-2}$. The Young's moduli and Poisson's ratios for the substrate materials[7] used in these measurements are given in Table 1.

Table 1
Mechanical Parameters for Low-expansion Sample Materials

Material	E_s (10^{10}N/m^2)	ν
Zerodur	9.1	0.24
Cervit C101	9.2	0.25
ULE	6.8	0.17

RESULTS

SAMPLE CURVATURE

Fig. 1 shows the curvature, as expressed by the Zernike coefficient C_3, as a function of temperature for sample plate number 9 (Cervit, 0.0042 inch thick coating). The data show that (a) the rate of change of curvature with temperature is lower in 1988 than in 1982, and (b) the plate is less concave (C_3 is less negative) in 1988 than in 1982. The same behavior was observed in the other coated plates. To determine the time dependence of the stress we linearly extrapolated the values of C_3 for each plate, measured at different temperatures, to a single temperature, using the measured values of dC_3/dT for the 1982 and 1988 time periods. Fig. 2. shows the values of C_3 for plate 9, extrapolated to 34°C, as a function of time. The slope $dC_3(34)/dt$ is positive, confirming the observation from Fig.1 that the plate became less concave with time. The same behavior is found for the other coated plates.

For comparison we measured the curvature of an uncoated Cervit sample (plate number 6). Unlike the others, this plate was not acid etched after its polished face was ground. No significant variation of C_3 with temperature or time was observed, as is expected for the uniform, low-expansion materials used in this study.

COATING STRESS

The behavior of the coating stress for the six coated samples is shown in Table 2.

1	2	3	4	5	6	7	8	9	10	11
Plate	Material	Coating Thickness	Stress σ_0@73°F ($10^7 Nm^{-2}$)		$d\sigma/dT$ ($10^5 Nm^{-2}C^{-1}$)		$(1/\sigma_0)(d\sigma/dT)$ ($10^{-2}C^{-1}$)		$d\sigma/dt$ ($10^5 Nm^{-2}yr^{-1}$)	$(1/\sigma_0)(d\sigma/dt)$ ($10^{-2}yr^{-1}$)
		(.001 inch)	1982	1988	1982	1988	1982	1988		
4	Zerodur	6.25±0.6	2.17	1.36	-9.47	-6.03	-4.36	-4.43	-6.7	-3.10
7	Cervit	4.88±0.5	3.76	2.57	-10.60	-6.95	-2.81	-2.70	-13.9	-3.70
9	Cervit	4.20±1.1	3.07	2.23	-9.11	-7.27	-2.97	-3.26	-10.3	-3.40
11	Cervit	1.00±0.4	4.12	2.48	-13.40	-8.06	-3.24	-3.26	-12.7	-3.10
24	ULE	4.37±1.0	2.73	1.87	-12.10	-6.50	-4.41	-3.47	-3.9	-1.40
30	ULE	1.05±0.2	4.14	1.30	-13.60	-7.00	-3.29	-5.38	-16.5	-4.00
						Avg:	-3.5	-3.8		-3.1
						Std Dev:	0.7	1.0		

Table 2. Variation of coating stress in coated samples

Calculating the stress from the measured curvature requires a knowledge of the film thickness. This was determined by etching small portions of silver from the four corners of each sample and measuring the film thickness with a dial indicator at each. The uncertainties given in column 3 of Table 2 are the 95% confidence limits of the measurements, calculated with Student's t statistic.

The coating stress for each sample was less in 1988 than in 1982, as shown in columns 5 and 6. Columns 6 and 7 show that the rate of change of stress with temperature was less for each sample in 1988 than in 1982. The thermal expansion coefficient is proportional to initial stress, as indicated by the uniformity of the normalized coefficients $(1/\sigma_o)(d\sigma/dT)$ in columns 8 and 9. The average values for 1988 and 1982, approximately -3.7 percent per degree Celsius, do not differ significantly. Because this coefficient is independent of σ, its value is not affected by uncertainty in the coating thickness.

The rate of change of the coating stress is negative for all samples, as shown in column 10. The normalized rate of stress change $(1/\sigma_o)(d\sigma/dt)$ is quite uniform across the samples, with the exception of an anomalously low value for plate 24; the average rate of change of stress is -3.1 percent per year. To determine whether errors in temperature measurement between the 1982 and 1988 experimental periods could account for the observed stress relaxation, we estimate the temperature change that would be required to give the stress change measured over the approximately 6.5 year span of the experiment. Table 3 shows the total stress change $\Delta\sigma$ for each plate and the temperature change ΔT_{error} that would produce that change if the entire change were caused by thermal expansion at the 1982 rate (the most conservative value). The values of ΔT_{error} range between 2.1 °C and 8.5 °C, all much larger than the 0.5 °C maximum error in the temperature measurement. Therefore we conclude that the observed stress relaxation was greater than could be accounted for by temperature measurement errors.

Table 3
Temperature Error Budget and Zero-Stress Temperatures

Plate	$\Delta\sigma$(6.5 yrs) (10^5N/m^2)	ΔT_{error} (°C)	T(σ=0) (°C)
4	-43.6	4.6	45.5
7	-90.4	8.5	59.8
9	-67.0	7.4	53.5
11	-82.6	6.2	53.6
24	-25.4	2.1	51.6
30	-107.3	7.9	41.4

The initial coating stresses measured in 1982, extrapolated to 23°C, are between 2×10^7 and 4×10^7 N/m^2. If the expected stress at room temperature is calculated from the measured values of $d\sigma/dT$, roughly $-10^6 \text{Nm}^{-2}\text{C}^{-1}$, and one assumes a temperature change from 700°C to 23°C, one calculates a room temperature stress on the order of 7×10^8 Nm^{-2}C^{-1}. The apparent discrepancy between calculated and observed stress is explained by the fact that annealed silver has a yield stress σ_y of $(1-5) \times 10^7$ N/m^2[8]. The average of reported values[8] of σ_y is 3.5×10^7 N/m^2, in good agreement with the observed initial 23°C stress values.

EFFECT OF STRESS RELAXATION ON MASER FREQUENCY

To estimate the possible effect of coating stress relaxation on a maser's output frequency, we carried out a finite-element calculation of the change in cavity shape caused by a change in coating stress. If the endplates and cylinder are assumed to be unconstrained, then a change in coating stress of 1×10^6 N/m^2 (typical of the yearly relaxation rates observed in these experiments) in a coating thickness of 0.003 inches, typical for maser cavities, causes the rim of the endplate to move approximately 1.5×10^{-5} cm longitudinally, while the cylinder moves roughly 1.8×10^{-6} cm radially. The major effect is due to the endplate, whose distortion increases the effective (electromagnetic) cavity length L on the order of 1.5×10^{-5} cm (including both endplates, and assuming that the effective change in electromagnetic length corresponds to about half the rim motion of each endplate). For a cavity resonance frequency f_c and maser output frequency f_o, a typical maser has $df_c/dL = 9 \times 10^5$ Hz/cm and a pulling factor $df_o/df_c = 1/30000$; thus the estimated rate of change of maser frequency due to coating stress relaxation for an unconstrained cavity is on the order of $(1/f_o)(df_o/dt) \sim 3 \times 10^{-12}$/yr $\sim 9 \times 10^{-15}$/day, which is roughly an order of magnitude larger than the observed drifts.

Two phenomena tend to reduce the effect of coating stress relaxation on the maser frequency. First, in the maser the polished endplate surfaces are pressed against the cylinder ends by Belleville springs, with a total force of about 450 pounds. This constrains the cylinder and endplates to move together radially, since the mating surfaces do not slide, and reduces the tendency of the endplate rim lift from the cylinder (curl). If the cylinder and endplates were solidly attached to each other, the endplate distortion due to coating stress change would be reduced by about a factor of 10 from the unconstrained values, and would be opposite in sign to the cylinder distortion, thus reducing the maser frequency shift by at least an order of magnitude. In reality, the cylinder and endplates are prevented from sliding against each other, but the clamping force is not enough to eliminate edge curl entirely. Therefore the estimated frequency shift is expected to be reduced from the unconstrained value calculated above by a factor of perhaps 3 to 10.

The second mitigating consideration is the fact that in operating SAO masers the cavity is maintained at a temperature of 50°C. Since raising the coating temperature above room temperature reduces the tensile stress, as is seen in Fig. 1, a higher ambient temperature also reduces the rate of stress relaxation. Table 3 shows the temperature at which the coating stress for each sample is expected to be zero, based upon the average 1988 stress at 23°C and the measured temperature coefficient for each sample. The values of $T(\sigma = 0)$ lie between 41°C and 60°C. Thus we can expect that maintaining the cavity at 50°C would reduce stress-induced maser frequency shifts considerably below the values estimated from the measurements made for a 23°C holding temperature. The combined effects of endplate constraint and 50°C holding temperature might reduce the frequency drift rate by one to two orders of magnitude, to between 1×10^{-15}/day and 1×10^{-16}/day, a range on the order of, to somewhat lower than, observed drift rates.

RELIEVING COATING STRESS

It appears possible to reduce the coating stress substantially for any particular holding temperature by appropriately precooling the sample or cavity. If the sample is cooled from an initially tensile state until the silver yields, and is then reheated to its original temperature, the final stress will be reduced. This effect can be seen in Fig. 3, which shows the bending of plate 9 as a function of time during the 1988 measurement period. When the plate was heated from 34°C (93°F) to 51°C (124°F) and returned to 34°C, its final shape was more concave than it was initially, $C_3(34°C)$ changing from -1.37λ to -1.80λ. Similar behavior was observed for the other coated plates. Cooling is expected to produce the opposite stress change. Such behavior was observed when a sample was cooled to 77°K and rewarmed to room temperature.

These observations suggest a technique for determining whether stress relaxation plays a significant role in the frequency drift of operating masers, as well as a method for minimizing such an effect. A maser cavity could be precooled to a temperature, roughly 0°C or lower, such that rewarming to 50°C would place the coating in compressive stress. A long-term drift of the oscillating maser toward lower frequencies would indicate the influence of stress relaxation. Such relaxation could then be reduced, or even reversed, by heating the maser, using its internal temperature-control heaters, by approximately 30°C, and returning it to its usual temperature.

CONCLUSIONS

The measurements described here show that (a) the internal stress in silver coatings bonded to low-expansion substrates relaxes at a rate of approximately 3 percent per year, and (b) the stress varies with temperature at a rate of approximately 3.6 percent per degree Celcius, with the thermal expansion coefficient decreasing with time as the internal stress decreases. Estimates of relaxation-induced frequency shifts, based on finite-element stress calculations, indicate that stress relaxation is capable of producing frequency drifts of the order of magnitude of those observed in masers, but that in any particular situation the stress effect may be less than observed drifts. It is possible to reduce the coating stress for any final temperature by appropriate precooling or preheating of the maser cavity. Such a technique should make it possible to measure the magnitude and sign of stress-induced frequency drifts, and to minimize any such effects.

ACKNOWLEDGEMENTS

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APPENDIX

The computer curve-fitting program expresses the three-dimensional deflection of a sample in terms of Zernike polynomials as follows:

$$y(r,\phi) = C_1\left(\frac{r}{r_o}\right)\cos\phi + C_2\left(\frac{r}{r_o}\right)\sin\phi + C_3\left[2\left(\frac{r}{r_o}\right)^2 - 1\right] \tag{A.1}$$

Here r is measured from the center of the rectangular sample, r_o is the distance from the center to the corner of the rectangle, and ϕ is the azimuthal position measured from the long axis of the rectangle. For variations parallel to the long axis, $\phi = 0$ and $x = r\cos\phi = r$, giving

$$y(r,0) = y(x) = C_1\left(\frac{x}{r_o}\right) + C_3\left[2\left(\frac{x}{r_o}\right)^2 - 1\right] \tag{A.2}$$

The curvature $K(x)$ of the function $y(x)$ is given by[9]

$$K(x) = \frac{d^2y/\,dx^2}{\left[1 + (dy\,/\,dx)^2\right]^{3/2}} = \frac{4C_3}{r_o^2\left[1 + \left(\frac{C_1}{r_o} + \frac{4C_3x}{r_o}\right)^2\right]^{3/2}} \tag{A.3}$$

and the curvature at the center of the sample, $K_o \equiv K(x=0)$, is

$$K_o = \frac{4C_3}{r_o^2\left[1 + (C_1/r_o)^2\right]^{3/2}} \tag{A.4}$$

For eqs. A.3 and A.4 to have meaning, all quantities must be measured in the same units. The coefficients $C_1 - C_3$ are on the order of several wavelengths λ of 6328Å light, and

r_o = 5.17 cm=8.2×10⁴λ, so $(C_1/r_o)^2 \sim 10^{-10} \ll 1$ and can be neglected in Eq. A.4. Therefore the central curvature of the sample is proportional to C_3:

$$K_o = \frac{4C_3}{{r_o}^2} \tag{A.5}$$

In a similar manner, the curvature of the parabola described by Eq. 1 is

$$K = 2\sigma \frac{3(1-\nu)}{E_s} \frac{t_f}{{t_s}^2} \tag{A.6}$$

Comparison of Eqs. A.5 and A.6 yields the result given in Eq. 2.

REFERENCES

1. D. Kleppner, H.M. Goldenberg, and N.F. Ramsey, "Theory of the hydrogen maser." *Phys. Rev.* **126**, 603 (1962)

2. S.F. Jacobs, "Dimensional stability measurements of low thermal expansivity materials using an iodine stabilized laser." *Proc. 2nd Frequency Standards and Metrology Symposium*, p. 269 (1976).

3. E.M. Mattison, R.F.C. Vessot, and S.F. Jacobs, "Properties of low-expansion materials for hydrogen maser cavities." *Proc. 39th Annual Frequency Control Symposium,* pp. 75-79 (1985).

4. Zygo Corporation, Middlefield, Conn., Model 1.

5. Wyco Corp, Tucson, Arizona, Wyco Interferometer Software Package (WISP).

6. D.S. Campbell, "Mechanical properties of thin films." In Handbook of thin film technology, L.I. Maissel and R. Glang, eds.,pp. 12-3–12-50 (McGraw Hill, 1970).

7. ULE titanium silicate, code 7971, brochure LEM-ULE-2/72, Corning Glass Works, Corning, New York (1972)
   Zerodur transparent glass ceramics, Schott Optical Glass Inc., Duryea, Pa (undated).
   Cer-Vit material for reflective optics, brochure RO-3 3-69, Owens-Illinois, Inc., Toledo, Ohio (1969).

8. J.L. Everhart, W.E. Lindlief, J. Kanegis, P.G. Weissler, and F. Siegel, Mechanical Properties of Metals and Alloys, National Bureau of Standards circular C447, U.S. Government Printing Office (1943).

9. A.E. Taylor, Advanced Calculus, p. 40. (Ginn, 1955).

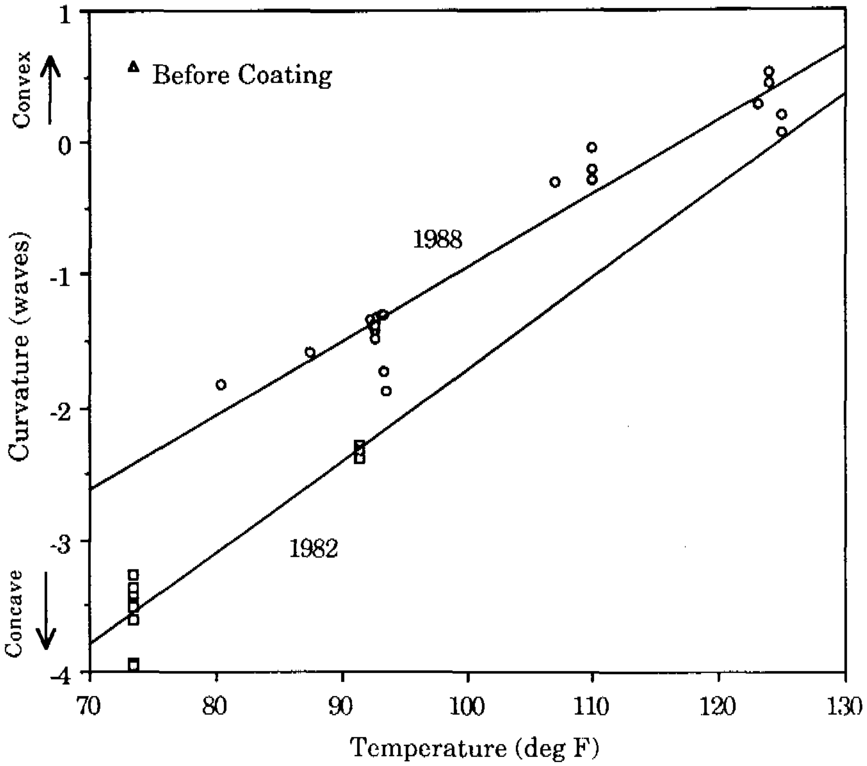

Figure 1. Plate 9 curvature as a function of temperature.

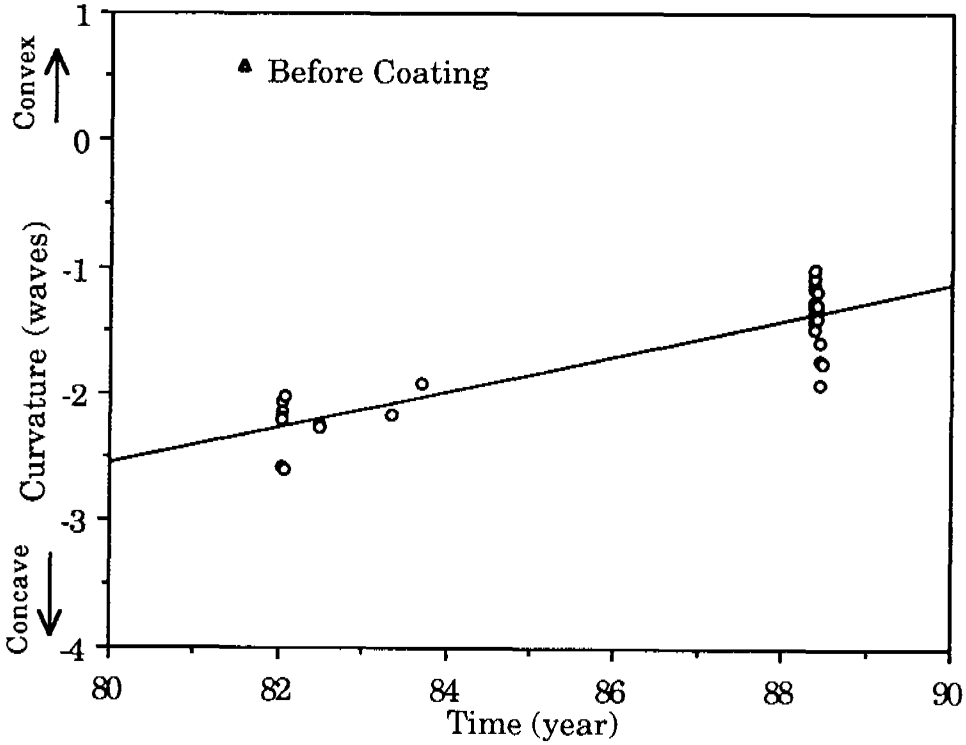

Figure 2. Plate 9 curvature, extrapolated to 34^{o}C, as a function of time.

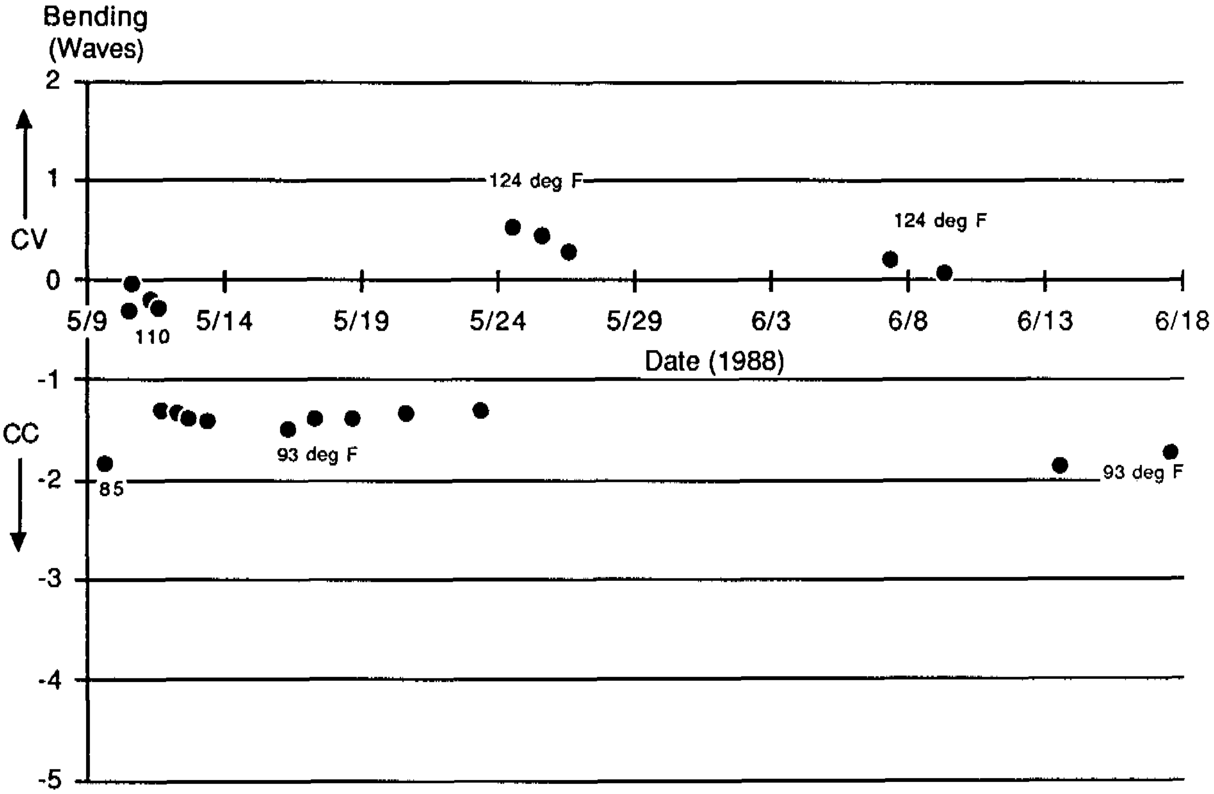

Figure 3. Plate 9 curvature as a function of time, 1988.

QUESTIONS AND ANSWERS

KEN UGLOW, UGLOW ELECTRONICS: What would be the hazards of coating both sides of the ceramic? Would there be problems with resonance between the two surfaces in the ceramic?

DR. MATTISON: There are no hazards. In fact, it might give further RF shielding. It might be beneficial.

DR. JOHN DICK, JPL: Do you have a mechanical or mechanistic explanation for the change of temperature coefficient with time?

DR. MATTISON: The temperature coefficient should be proportional to the effective Young's modulus of the coating. As time progresses, because the coating is basically particulate, the effective Young's modulus decreases.