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Aging of Dielectric-coated Aluminum in Deionized water

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Introduction

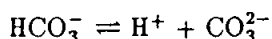
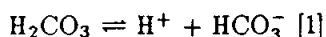
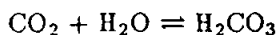
According to present theory, the nuclear processes in the sun give off vast quantities of neutrinos. Experiments confirm the production of these particles, but fail to detect the quantity predicted by theory. The most recent experiments have found a maximum of two thirds the expected number of neutrinos.

The Sudbury Neutrino Observatory is being constructed to accurately determine the neutrino flux from the sun. The detector consists of 1000 tonnes of heavy water. Neutrinos entering the heavy water occasionally react in such a way as to produce Cerenkov radiation. This radiation is then detected by photomultiplier tubes surrounding the heavy water. To increase the detector efficiency, each photomultiplier tube is surrounded by a light reflecting concentrator composed of dielectric-coated aluminum "petals". Their design is shown in figure nine. These petals must be able to withstand the aqueous environment of the observatory for the 10 year life of the facility.

In previous tests, the dielectric-coated petals of aluminum have exhibited degradation after simulated long exposure to deionized water. Measurements of the reflectance of these degraded petals showed an interference pattern caused by the oxidation of the reflective aluminum layer, leaving a $2\mu\text{m}$ transparent dielectric layer on the aluminum substrate. A series of new tests have been performed to determine what properties of the deionized water are causing the degradation, and whether the degradation is likely to occur in SNO itself.

Chemistry of the Deionized Water

The deionized water for the experiment was produced with a Barnstead E-pure filter system. This system removed ions, including the ions present in the carbonate chain:



This equilibrium is dominated by dissolved $\text{CO}_2(\text{g})$, but the cycling action of the filter combined with the fast (0.1 second) [3] return to equilibrium of this system removes all of the carbonates and CO_2 present. Deionized water is produced with a pH of 7.00(05), and a conductivity of $0.07(02)\mu\text{S}/\text{cm}$.

Tests on the Deionized Water

Several tests were performed on the Deionized water. In the first, conductivity was studied at various depths after a set time. Figure one shows the conductivity at different depths after 70 minutes exposure to the atmosphere.

The pH and the conductivity of the DI water were studied over time when exposed to air, N_2 gas, CO_2 gas, and CO_2 -free air. Diagrams two through four show pH vs. Conductivity in CO_2 . Figure five shows the conductivity of DI water with time as Nitrogen was bubbled through the water. The conductivity was recorded over time for each sample. CO_2 -free air was also used as a cover gas for one run.

Figure six shows conductivity over time with CO_2 as a cover gas, and figure seven shows conductivity over time for a sample exposed to the atmosphere. This sample was covered to exclude dust, but was allowed contact with the air.

The dissolved Oxygen content of the DI water was also studied to see how it varied with varying Carbonate concentrations.

In the second part of the experiment, the aluminium petals were exposed to several different environments. A vacuum oven was attached to several different gas cylinders so that the cover gas on the petals immersed in deionized water could be changed and maintained at a fair level of purity. The 90°C . run for seven days was equivalent to one year in SNO. This is due to the ther-

modynamic doubling of reaction rates per ten degrees C. The 40°C. run was equivalent to two thermodynamic years in SNO.

The first test involved twenty petals being exposed to a CO₂ saturated solution for four weeks at room temperature. Three runs were performed over four weeks at 40°C. The first consisted of 30 petals exposed to bubbled nitrogen. The next consisted of 17 petals in DI water exposed to the room air. The last consisted of eight petals exposed to CO₂ saturated water. The petals were sampled every week for the four weeks.

Three higher temperature runs were performed. They consisted of one week runs in the vacuum oven in an atmosphere of CO₂, CO₂-free air, and nitrogen. The temperature was 92°C.

One petal was exposed to saturated NaOH solution in order that the degradation process could be observed.

Analysis

Diffusion of CO₂ in 24°C DI water

Upon exposure to the atmosphere, CO₂ reenters the water in accordance to Henry's law:

$$[CO_2] = K_H P_{CO_2} [1]$$

K_H is Henry's constant, $10^{-1.5}$ at 25°C.; P_{CO_2} is the partial pressure of CO₂ in atmospheres, and concentration in moles/ℓ. The hydrogen ion concentration in the water can be written as:

$$[H^+]^2 = K_{a1} K_H P_{CO_2} + \dots [1]$$

where K_{a1} is the first ionization constant of the Carbonate system. It has a value of 1.7×10^{-4} . In terms of pH,

$$pH = 3.91 - \frac{1}{2} \log P_{CO_2} + \dots [1]$$

By observing the conductivity, which is linked to dissolved ion content and thus the Carbonate content, at different depths, a diffusion constant for CO₂ was found. The data were fitted to Fick's solution of the equation of diffusion:

$$C = \frac{A}{\sqrt{t}} e^{-\frac{x^2}{4Dt}} [2]$$

The constant D was found to be $1.554(57) \times 10^{-5} \text{m}^2/\text{s}$.

Approach to equilibrium in several gaseous environments

The data in figures two to four was taken at three cm depth shows an exponential nature, and so were fitted to

$$pH = Ae^{BS} + pH_{\infty}$$

where S was the conductivity. It was found that A was 3.7(8) and B was -0.44(14)cm/μS. pH_∞ was found to be 3.86(01)

With a cover of CO₂ free air, the conductivity stayed at 0.31μS/cm. for 30 minutes, falling to 0.27μS/cm. over the next 60 minutes. In the N₂ covered runs, the conductivity rose to 0.45μS/cm. in each case. With CO₂ as a cover gas the conductivity rises rapidly, as seen in figure eight. The conductivity peaked in all trials at 20(2)μS/cm The pH approached 3.86, slightly different from the 3.91 quoted in the literature. This could be explained by the CO₂ content being higher in the room than standard air. When regular air was used as a cover, conductivity rose over time in an exponential manner. Fitting to an exponential,

$$S = 1.50(05) - 0.90(05)e^{-0.024(03)t}$$

time in hours.

Effect of gas cover on dissolved oxygen

Dissolved Oxygen activity remained fairly constant at between 40% and 50% with the oxygen per liter in the 5 to 8mg/l range. In an atmosphere of pure CO₂ or N₂ this value decreased.

Results of the Dielectric-Aluminum Tests

All of the room temperature CO₂ samples showed pitting and had patches of a whitish nature on the surface. This white powder rubbed off to leave the underlying surface intact. This white powder appeared within the first week, reducing the reflectivity from five to ten percent. It could have been Aluminum Oxide from the back of the petals, or be from a biological source. It also could have been produced from the container used in the tests. No further degradation from this source occurred. Six samples showed failure of the underlying layers. One petal failed across the whole surface. The others failed only at corners, the area of failure ranging from 1 cm² to 3 cm².

Of the eight petals tested at 40°C in saturated CO₂, one failed. The others showed no degradation.

There were no failures in the Nitrogen 40°C batches. The Nitrogen samples were coated with a white precipitate similar to that found in the CO₂ run, except thicker. It was easily removable and caused no long term damage to the petals.

Three of the 40°C air test petals failed. The rest showed faint signs of the white precipitate present on the Nitrogen samples. The failures were not complete, ranging from one quarter to one half of the petal surface.

The vacuum oven was used to expose nine petals to CO₂ with no Oxygen at 92°C for 160 hours. The water achieved a pH of 3.95 due to interaction with the CO₂. Of the nine petals, seven were not affected, having reflectances of within three percent of the standard. A random scan of new petals shows the same spread. The other two petals were badly failed, as seen in figure nine.

The same test was repeated with CO₂ free air replacing the CO₂. Of the nine samples tested, there were no failures. All were within three percent of the standard untreated sample.

The Nitrogen test has not yet been completed.

Exposure to NaOH solution

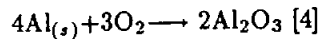
Substantial damage occurred to a petal immersed in NaOH for one half hour. At first the petal showed no signs of deterioration, but bubbles, soon began to form under the protective coating along the edges and on the surface wherever pit marks allowed. The coating along the edge then quickly cracked off, allowing attack of the underlying material. Within twenty minutes the petal had failed.

Atmosphere	Temp(°)	Samples	Failures
CO ₂	90	9	2
CO ₂ -free air	90	9	0
N ₂	42	30	0
Air	42	17	3
CO ₂	42	8	1
CO ₂	24	20	1

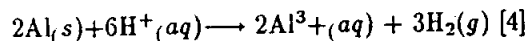
Table 1: Aluminum Aging Test Results

Aging Processes involved

Several possible processes could be at work. The reaction



could be causing the whitish surface deposits on the petals. However, upon polishing the petals were restored to their original condition. The white deposit is possibly from an external source, such as the container the test was conducted in. The more serious damage could be a result of the reaction



The acid involved was the carbonic acid formed in the water upon exposure to the atmosphere.

Conclusion

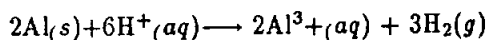
Deionized water exposed to air establishes equilibrium with the Carbonate ion chain. This causes the PH of the deionized water to fall according to

$$pH = pH_{\infty} - \frac{1}{2} \log P_{CO_2} + \dots$$

where pH_{∞} was found to be 3.86(02).

When placed in deionized water with a pH of 3.86, the dielectric-coated aluminum experienced 4 failures in twenty petals, at room temperature(24°C.),

after four weeks. There was one failure out of eight petals at 40°C after four weeks, and two failures out of nine petals at 90°C. after seven days. The reaction responsible is:



This reaction was not detected in environments with pH of 7.0 even at 90° Exposing the samples to CO₂ free air environment stopped degradation. No failures were found in petals exposed to a cover gas of Nitrogen after four weeks at 40°C

These results suggest that in the SNO environment at 8°C and with a pH of near 7.00, no failure of the nature seen in these tests will occur in a ten year period.

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5. Conductivity over time bubbling N₂ through DI water.
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7. Conductivity over time in DI water exposed to air.
8. Reflectances of failed and unfailed Aluminum petals.
9. Schematic of the Dielectric-coated Aluminum petals.

References

- [1] James M. Butler *Carbon Dioxide Equilibria and Their Applications* Addison-Wesley, 1982.
- [2] J Crank *Mathematics of Diffusion* Clarendon Press: Oxford. 1956. pp. 9-15.
- [3] James M. Butler *Solubility and PH Calculations* Addison-Westley, 1963. pp. 70.
- [4] Ralph H. Petrucci *General Chemistry* Macmillan. pp. 495-497

Figure One

Conductivity vs depth
After 70 minutes

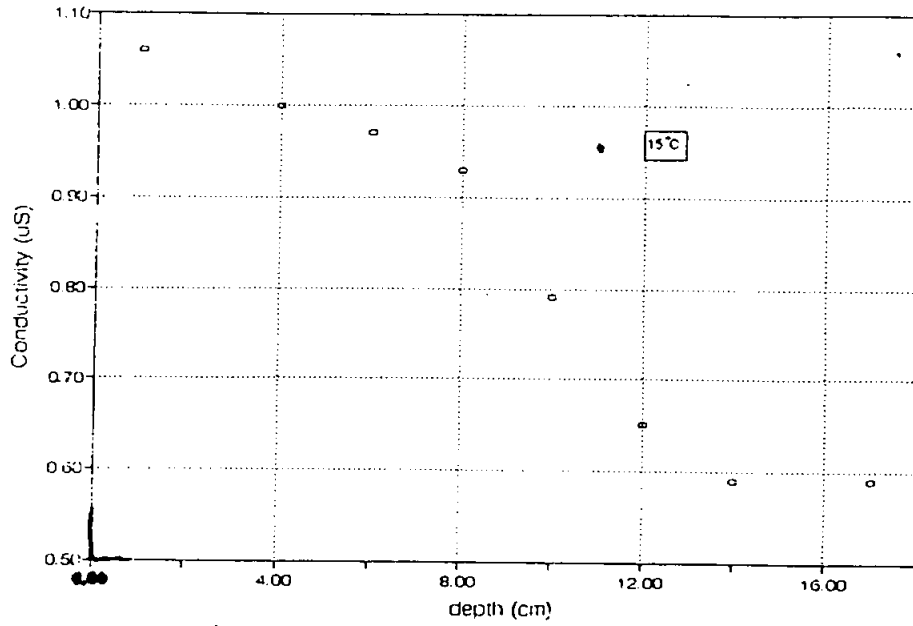


Figure Two

PH vs. Conductivity
IN DI water

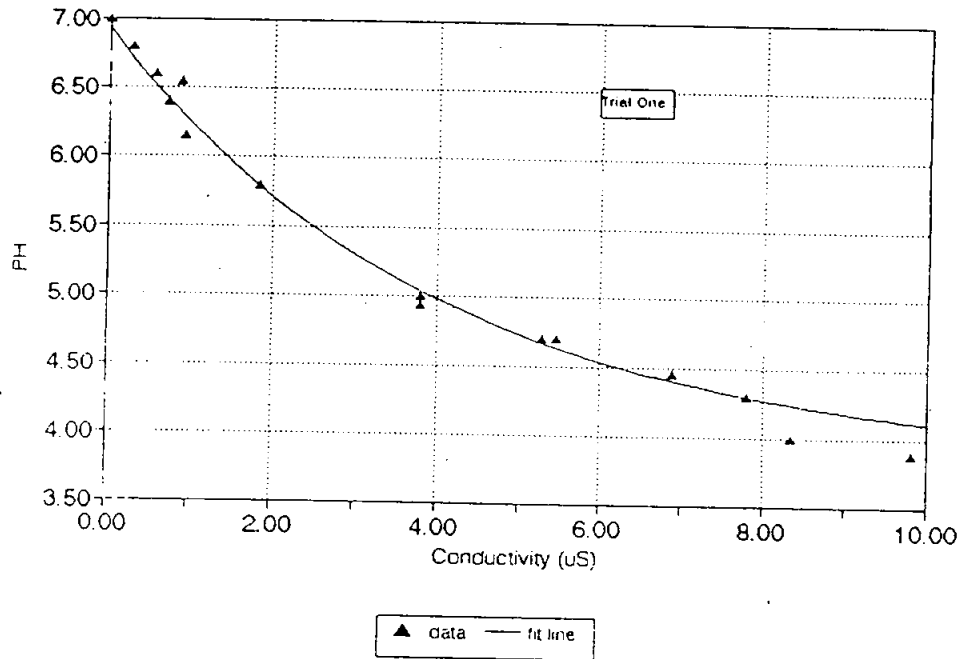
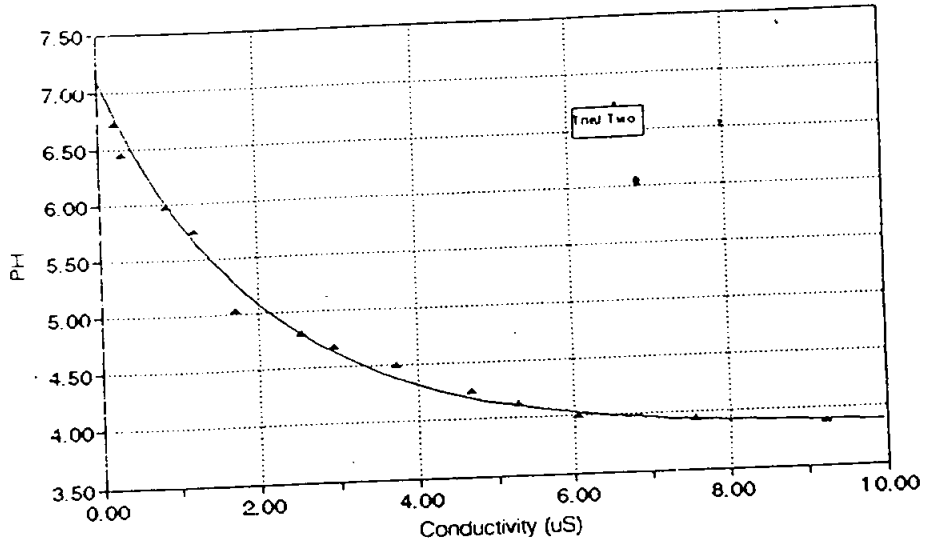


Figure Three

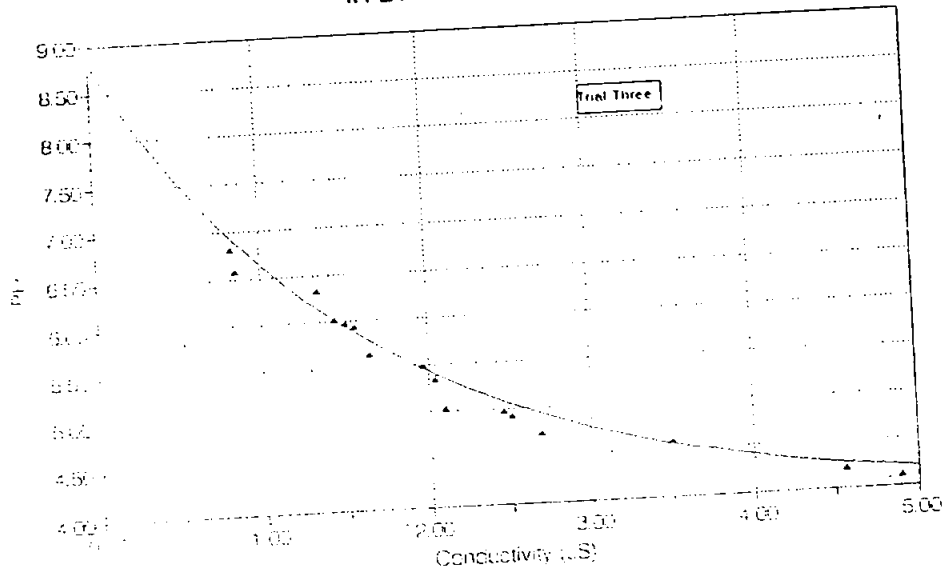
PH vs. Conductivity
In DI water



▲ Data — Fit

Figure Four

PH vs. Conductivity
In DI water



▲ Data — Fit Line

Figure Five

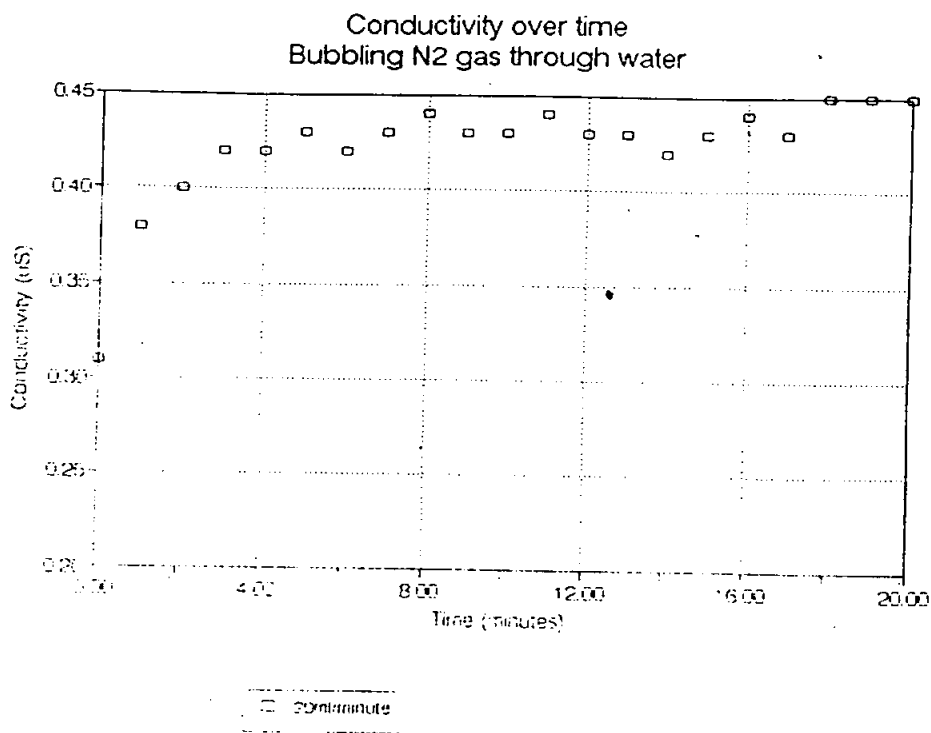


Figure Six

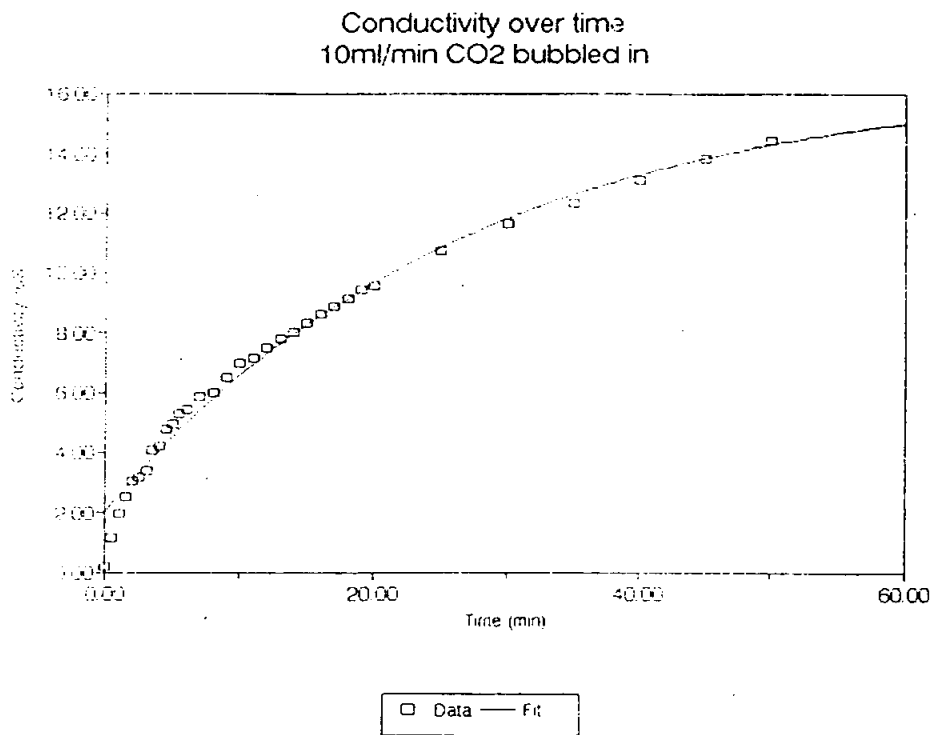


Figure Seven

Conductivity at 15 °C
3cm depth

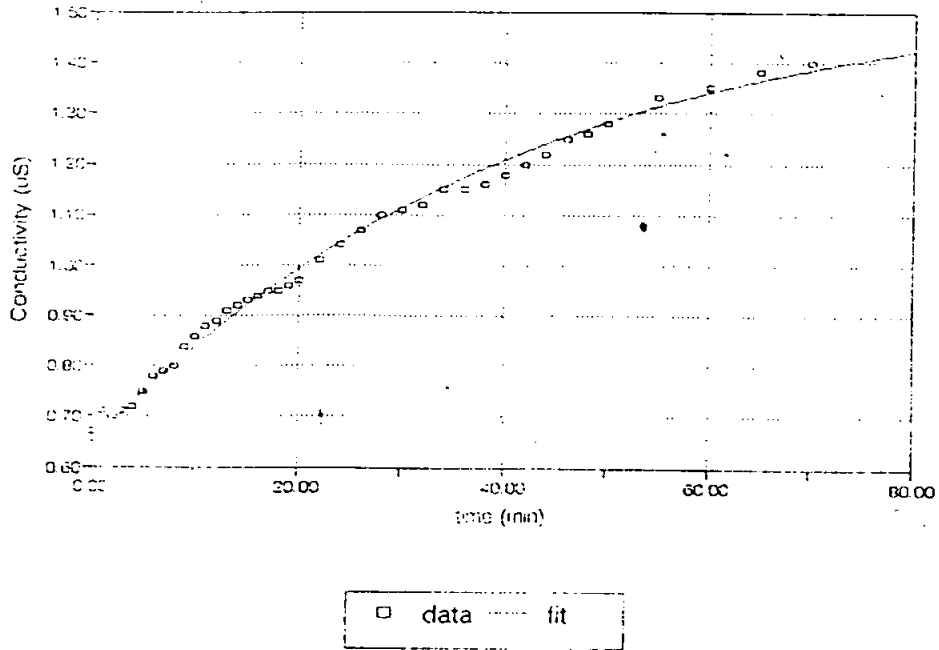
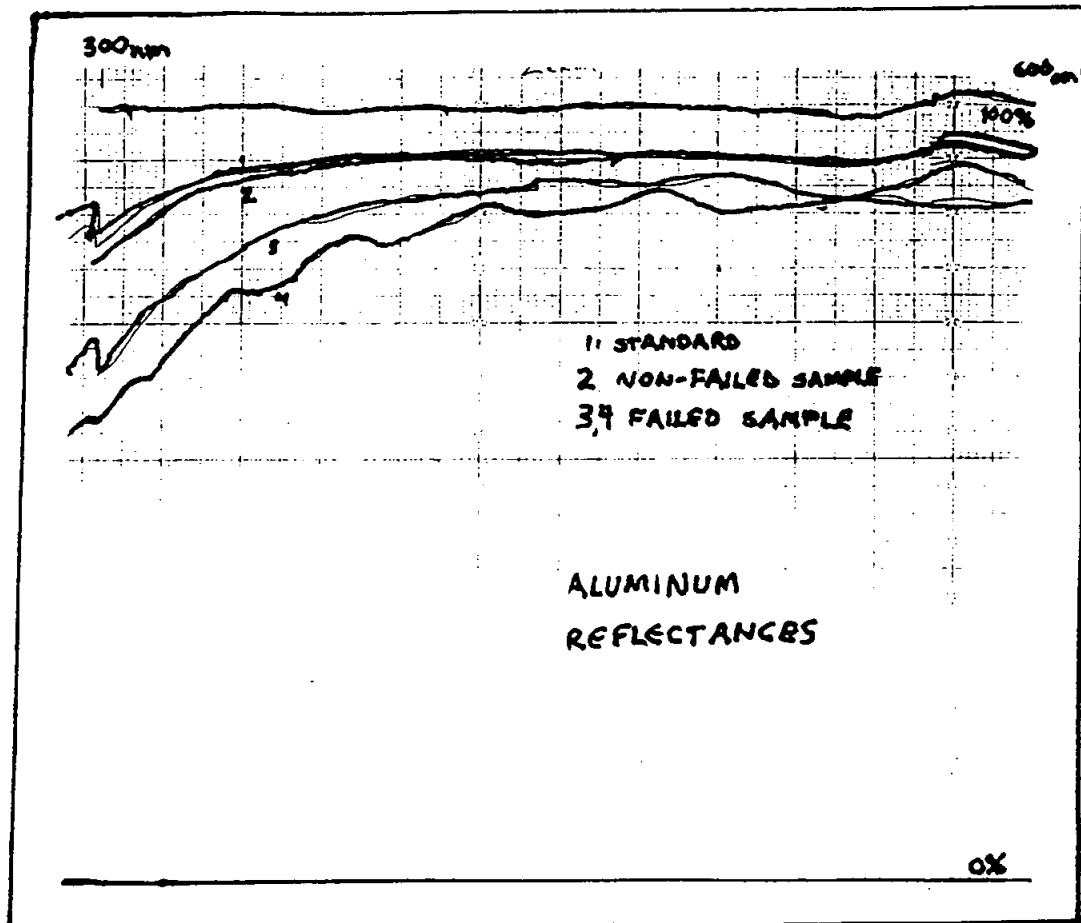


Figure Eight



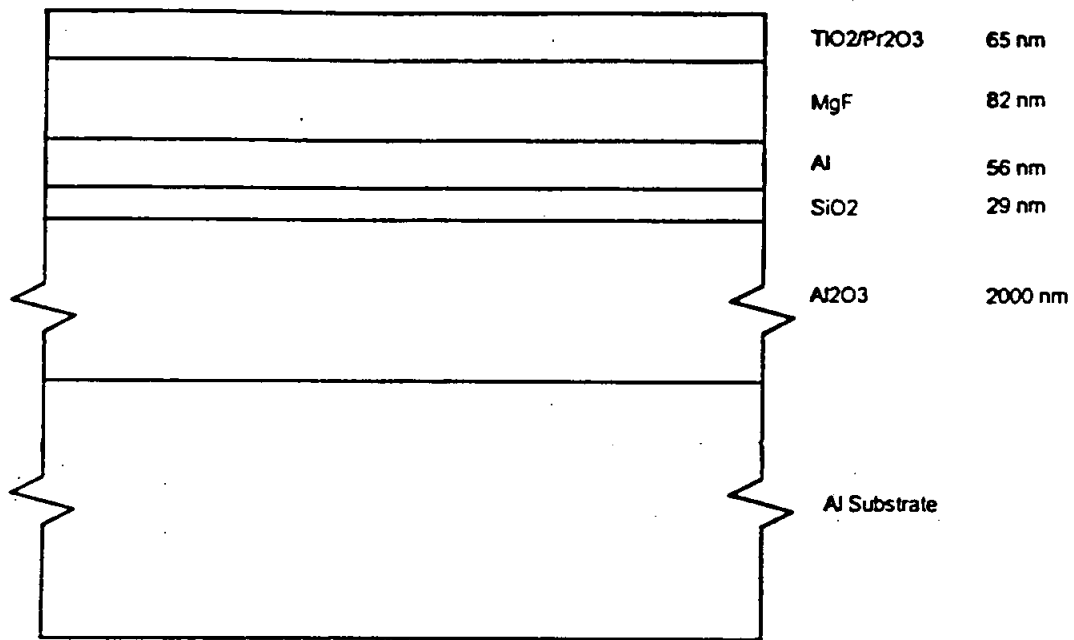


Figure 3.9: DCA layers.