### On the Line Q Degradation in Hydrogen Masers

L. G. Bernier, G. Busca, H. Schweda Observatoire de Neuchâtel, Switzerland

#### Abstract

In hydrogen masers, the atomic resonance quality factor is largely determined by the properties of the Teflon coating on the quartz storage bulb. Normally a good Teflon coating will last many years. On the other hand, there may be a relatively fast degradation of the quality factor if the Teflon coating is bad. This paper updates a series of observations and measurements performed on an hydrogen maser that had successively a bad and a good Teflon coating.

#### 1.0 Introduction: A Pathological Case

In hydrogen masers, the atomic resonance quality factor is largely determined by the properties of the Teflon coating on the quartz storage bulb. Normally a good Teflon coating will last many years and will show an extremely slow degradation of the atomic quality factor. On the other hand, once upon a time the Teflon coating happens to be "bad" which is characterized by a reasonable initial value of the atomic line quality factor followed by a fast degradation. The physico-chemical composition and structure of Teflon coatings is not well known. Empirical evidence shows that the atomic hydrogen consumed during normal maser operation plays a role in the degradation mechanism of a bad coating [1] and that the curing process is as important as the raw material in the preparation of a successful Teflon coating. This paper updates a series of observations and measurements performed on our hydrogen maser EFOS-7, operated in Sweden at Onsala Space Observatory, that had successively a bad and a good Teflon coating [2].

#### 2.0 The Effect of Air on a Bad Teflon Coating

In the past, we observed once that any intervention on a certain maser would temporarily cure its amplitude decay problem, whatever the intervention was. It was finally suspected that the simple fact of exposing the storage bulb to air, during the intervention, would temporarily improve the quality factor. More recently this past observation lead us to deliberately try the experiment on a maser that suffered a fast degradation of the line Q. The only intervention made on the maser between the 2 measurements of the quality factor reported below consisted of filling the maser with air and then

pumping down again. The atomic line quality factor was  $1.20 \times 10^9$  before and  $1.44 \times 10^9$  after exposure to air. The cure produced by exposure to air was temporary and the decay continued as before.



Figure 1 Atomic Line Quality Factor vs Time

# 3.0 The Time Behavior of a Bad Teflon Coating

The effect of a bad Teflon coating on the maser behavior was observed for several months. Figure 1 shows the evolution of the line Q starting just after the re-coating of the storage bulb. The origin of the time axis is the first day of oscillation. It can be observed that there is a decelerating degradation, during the first days, and then the degradation rate stabilizes. Figure 2 shows a linear regression of the linear part of the line Q degradation. The equation of the linear regression is as follows:  $Q = 1.9528 \times 10^9 - 3.7052 \times 10^6 t$  [day]. The relative degradation rate is 0.19 %/day. Figure 3 shows the amplitude of the maser signal versus time. By amplitude we mean the detected peak amplitude at the 5.7 kHz last IF in the receiver. Again there is a decelerating decay, at first, and then the rate of decay stabilizes. The amplitude steps are due to hydrogen pressure resettings. Figure 4 shows the linear part of the curve with the amplitude steps corrected by translation of the constant hydrogen pressure segments. A linear regression of the data points yields: A [V] =  $11.741 - 4.0735 \times 10^{-2} t$  [day]. The rela-

tive rate of decay is 0.35 %/day. Figure 5 shows the normalized frequency  $y(t) = \Delta v(t)/v_0$ . The beat frequency  $\Delta v(t)$  was measured by comparing the maser frequency  $v_0$  with the frequency of a reference maser.



A periodical spin-exchange tuning of the cavity showed that the microwave cavity was not drifting. The big frequency step on the curve is due to the initial spin-exchange tuning of the microwave cavity. The small steps are due to the imperfect resetting of the varactor voltage after each verification of the correct spin-exchange tuning. Figure 6 shows the y versus t curve with the frequency steps corrected by translation of the constant cavity tuning segments. The residual frequency change is approximately logarithmic. The analytic curve shown on the figure is given by:  $y(t) = -1.7693 \times 10-12 + 2.8426 \text{ LOG}(t \text{ [day]})$ . If the frequency change were due exclusively to the time varying cavity pulling effect associated with the line Q degradation, one would expect a linear drift. Thus the observed non-linear drift seems to indicate a wall shift evolution associated with the Teflon degradation.



Signal Amplitude vs Time

### 4.0 Discussion: Present Situation

The storage bulb of the same maser described above was re-coated and put back into operation with the same hydrogen dissociator as before. The signal is now higher (-104 dBm, i.e. 12.0 V amplitude peak at the 5,7 kHz last IF) for a smaller hydrogen flux (0.1 mBar of hydrogen in the dissociator, i.e.  $V_p = 6,5$  [V] at the pirani gauge output, with a  $\phi$  0.15 mm × 1.5 mm collimator). After several months of operation there is no sign of signal decay. This means that the bad coating was entirely responsible for the signal decay observed before. The fact that the signal is now stronger for a lower hydrogen pressure in the dissociator is a sign that, as expected, the threshold flux is lower with the good coating. The operating quality factor is now stabilizing at about Q =  $2.3 \times 10^9$  (with 0.1 mBar in the dissociator) with an initial value of Q =  $2.5 \times 10^9$  as shown on figure 7.



Signal Amplitude vs Time Corrected for Constant Hydrogen Pressure

# 5.0 Conclusion: Investigations at ON on the Teflon Coating

The properties of the coating and possible ways to test the Teflon before actual use in a maser are under investigation at Neuchâtel Observatory. From a practical point of view, we believe that it is equally important to control both the properties of the initial Teflon coating solution as well as the conditions of the drying and curing process if reliable coatings are to be produced.

For example, the thickness of the coating is determined by the concentration of the Teflon resin in the coating solution. The concentration may be estimated from a measurement of the specific weight of the commercial solution which is normally about 1.42 according to Du Pont. Our experience shows that the actual Teflon resin concentration may vary largely from sample to sample, simply because the solution has a tendency to separate when stored for some time. The solution is originally conditioned by Du Pont into 13 kg buckets. If a sample of the solution is poured from a large to a small container, which is always the case since a few cubic centimeters are sufficient for the coating of a storage bulb, the concentration of the sample is strongly dependent upon the storage time of the large

container if the solution is not perfectly mixed before pouring. On the other hand, the commercial solution cannot be stored for more than a few months because the residual of the initiator, left after the polymerization process, causes the solution to separate. Therefore it is not possible to select a good solution and keep it forever for the coating of future masers.



In conclusion there is a definite need for a method that would permit to determine the performance of a coating without actually testing it into an oscillating maser. The possibility of testing coating samples with Electron Spin Resonance (ESR), Infrared Spectroscopy (IS) and Photon Spectroscopy (XPS) is now under investigation at Neuchâtel Observatory. Preliminary results with ESR testing shows that there is a sizable difference in free electron spins between different Teflon samples. However we suspect that the differences are determined more by the curing process than by a difference of composition between different batches of the Teflon solution. A very tight control of all the parameters of the curing process would be necessary in order to demonstrate differences between different Teflon batches.



- Mattison E. M., Vessot R.F.C., Bain C., Wasserman S., Whiteside G. "Surface Interaction of Atomic Hydrogen with Teflon," *Proc. 41st Annual Symposium on Frequency Control*, Philadelphia, May 1987, pp. 95-98.
- [2] Bernier L.G., Busca G., "Some Results on the Line Q Degradation in Hydrogen Masers", 4th European Time and Frequency Forum, Neuchâtel, March 1990, pp. 713-714.

#### Acknowledgements

We want to thank Prof. Schweiger of the Laboratorium für Physikalische Chemie, ETH Zürich, for his ESR measurements on the Teflon samples and Joel Elldér of Onsala Space Observatory in Sweden for his field line Q measurements on the EFOS-7 maser.



t [day] Figure 7 Atomic Line Q with Good Coating

л

1