

Test of wall coatings for controlled moist air experiments

Hans J. Liebe and Vincent L. Wolfe

National Telecommunications and Information Administration, Institute for Telecommunication Sciences,
Boulder, Colorado 80303

David A. Howe

National Bureau of Standards, NBS 524, Boulder, Colorado 80303

(Received 7 May 1984; accepted for publication 16 June 1984)

Various hydrophobic surface treatments were investigated to facilitate high humidity (relative and absolute) experiments with a millimeter wave spectrometer. There were 17 different cases tested for adsorption and desorption behavior of a vacuum chamber, employing various combinations of metal surfaces (stainless steel, aluminum, brass), coating materials (electropolish, gold plate, Teflon, HMDS, silicone, lacquer), and surface-to-volume ratios (0.3 to 1.7 cm^{-1}). Test procedure and data are described together with a brief discussion of the findings. Trends are evaluated toward an effective reduction of the wall effect, which is a nemesis to all laboratory studies involved with polar gas molecules such as H_2O in air.

INTRODUCTION

Controlled laboratory studies of millimeter wave attenuation due to water vapor in air are performed using a Fabry-Pérot resonator mounted inside a spectrometer cell. Close to saturation ($\text{RH} > 75\%$) the cell surfaces tend to accumulate multiple layers of water molecules through adsorption. An equilibrium exists between the thickness of condensed water and the relative humidity; layers will evaporate (desorb) when the relative humidity is lowered. The RH and time-dependent water film on the resonator mirrors causes serious errors in attenuation measurements. Absolute vapor attenuation measurements, therefore, require that a surface passivation or coating procedure be used to minimize sorption effects.

Numerous studies have been made of assorted coatings' repellency to liquid water (i.e., rain),¹⁻⁵ but few have been concerned with hydrophobicity toward water vapor. One method of testing water repellency is measurement of drop contact angles.⁶ Vapor adsorption is usually characterized in terms of the amount adsorbed as a function of pressure at constant temperature. Since spectroscopic measurements can be made over a limited period of time, rates of adsorption are more important than the net amount adsorbed. Hence, the procedure employed has been to introduce a fixed amount of water vapor into the test chamber and then record changes in pressure with time $e(t)$, at constant temperature.

I. TEST PROCEDURE

Tests were performed using $3.3 \times 10^3\text{-cm}^3$ (3 1/2 quart) stainless-steel (SS 304) beakers. The setup is sketched in Fig. 1. The beakers were electropolished and coated with materials listed in Table I. Also tested were two larger chambers, one of stainless steel (Fig. 2) and one of aluminum, both untreated. The beakers were 18.10 cm in height and 7.78 cm in radius with walls 0.36 mm thick. The area of the baseplate was 190 cm^2 , resulting in a surface-to-volume ratio (S/V) of 0.37 cm^{-1} . The S/V ratios for the steel and aluminum chambers (see Table I) are much less than that of an existing

Fabry-Pérot interferometer,⁷ the performance of which prompted this study. Higher percentage sorption in the interferometer, as well as longer time constants for adsorption and desorption, indicate the importance of having the smallest surface area possible relative to the chamber's volume. Care should also be taken to eliminate anything that would

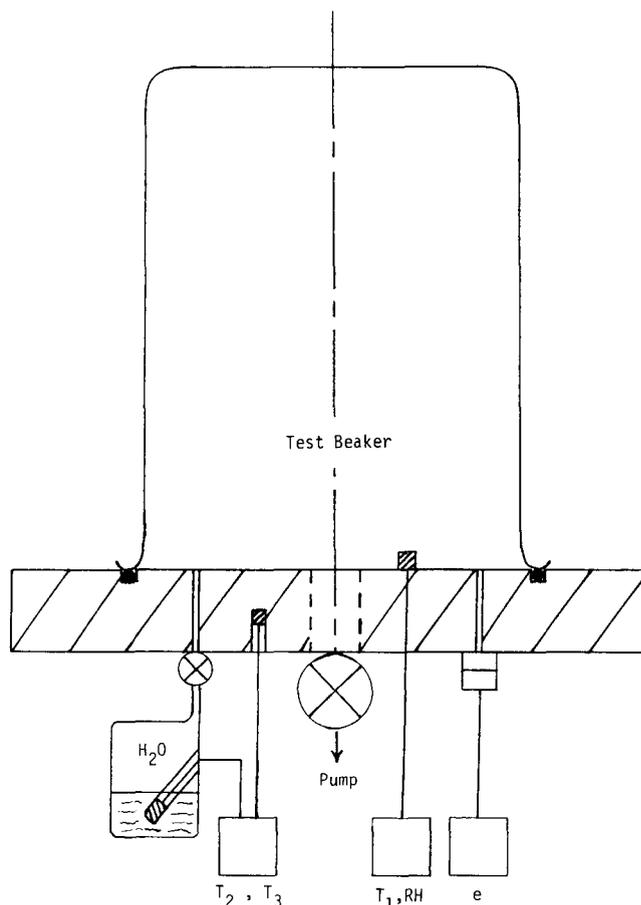


Fig. 1. Vacuum station showing test beaker, temperature (T_1 , T_2 , T_3), relative humidity (RH), and pressure (e) sensors, pump connection, and water vapor generator.

TABLE I. Results of water vapor sorption tests for various coating substances and configurations.

| Coating material | Percent sorption $1 - e/e_0$ [$e_0 = 2.4$ kPa (18 Torr) at 23.0 °C] | Monomolecular layers (cube with length = 1.9 Å) | Time response | |
|---|---|--|---|---|
| | | | Adsorption time constant τ_a | Desorption time constant τ_d |
| (a) Test beakers (Fig. 1) | | | | |
| SS 304, electropolished | % 1.6 (Reference) | 35 | min 3.0 | min 8.5 |
| Hexamethyldisilazane: HMDS (0.5 ml/application) | | | | |
| 1 applic. (3.95×10^{-4} ml/cm ²) | 1.35 | 29 | 3.7 | 23 |
| 2 applic. (7.90×10^{-4} ml/cm ²) on SS 304 | 1.5 | 33 | 4.5 | 62 |
| 1 applic. on gold-plated SS 304 | 1.2 | 26 | 5.0 | 4.9 |
| 1 applic. on 12.9/12.1/75.0 ^a Teflon FEP 120 | 1.5 | 33 | 5.2 | 21 |
| Teflon FEP 120 (DuPont) ^b | | | | |
| 1 coat 12.9/12.1/75.0 ^a (~10 μm thick) | 1.05 | 23 | 2.9 | 17 |
| 2 coats 16.34/12.66/71.00 ^a (~25 μm thick) | 2.9 | 64 | 3.8 | 90 |
| Parylene "C" (Union Carbide) ^b | | | | |
| 18 μm on polished SS 304 | 1.65 | 37 | 2.2 | 9.7 |
| 25 μm on acid-etched SS 304 | 1.8 | 40 | 4.3 | 13 (see Fig. 3) |
| Silicone SR 240 (G.E.) ^b | | | | |
| (2.3×10^{-3} ml/cm ²) | 1.9 | 42 | 3.3 | 9.0 |
| Gold-electroplated SS 304 | | | | |
| | 2.3 | 50 | 4.5 | > 10 |
| Clear lacquer (N.A.P.) ^b | | | | |
| 1 coat (baked at 50 °C) | 4.0 | 88 | 4.0 | 120 |
| (b) Spectrometer chambers | | | | |
| Composite chamber (brass, steel, silver), untreated ^c | | | | |
| $V = 4340$ cm ³ ($S/V = 1.77$ cm ⁻¹) | 19.5 | 68 | 120 | 300 |
| Aluminum chamber, untreated | | | | |
| $V = 8980$ cm ³ ($S/V = 0.31$ cm ⁻¹) | 2.6 | 52 | 5.3 | 100 |
| Stainless-steel chamber, ^d electropolished | | | | |
| $V = 10630$ cm ³ | | | | |
| Empty ($S/V = 0.31$ cm ⁻¹) | 0.95 | 27 | 5.5 | 22 |
| With SS screen roll ($S/V = 0.50$ cm ⁻¹) | 1.2 | 20 | 5.6 | 24 |
| With mirrors, stands (Fig. 2) ($S/V = 0.46$ cm ⁻¹) | 1.8 | 33 | 9.7 | 67 |

^a Teflon FEP 120 dispersion/Triton X100/water = mixing ratio by volume.

^b Reference 18.

^c Reference 7.

^d Reference 8.

remove water from the system (e.g., dirt, particulates, small crevasses, corner areas).⁹

The beakers were connected to a vacuum station with attached temperature, pressure, and humidity probes. The aluminum base (20% of the total surface area) was sandblasted, electrocleaned, baked, and coated with Teflon. Water vapor was introduced into the evacuated beaker (10^{-2} Pa

for 1 min to a pressure approaching saturation [$e_0 = 2.4$ kPa (18.0 Torr) at 23.0 °C]. The water vapor was allowed to stand for 1000 s while the adsorption rate (pressure decrease) was measured isothermally. The remaining water vapor was then evacuated from the chamber in a 1-min period, followed by measuring the desorption rate (pressure increase) over another 1000-s interval. Sorption limits were approximated

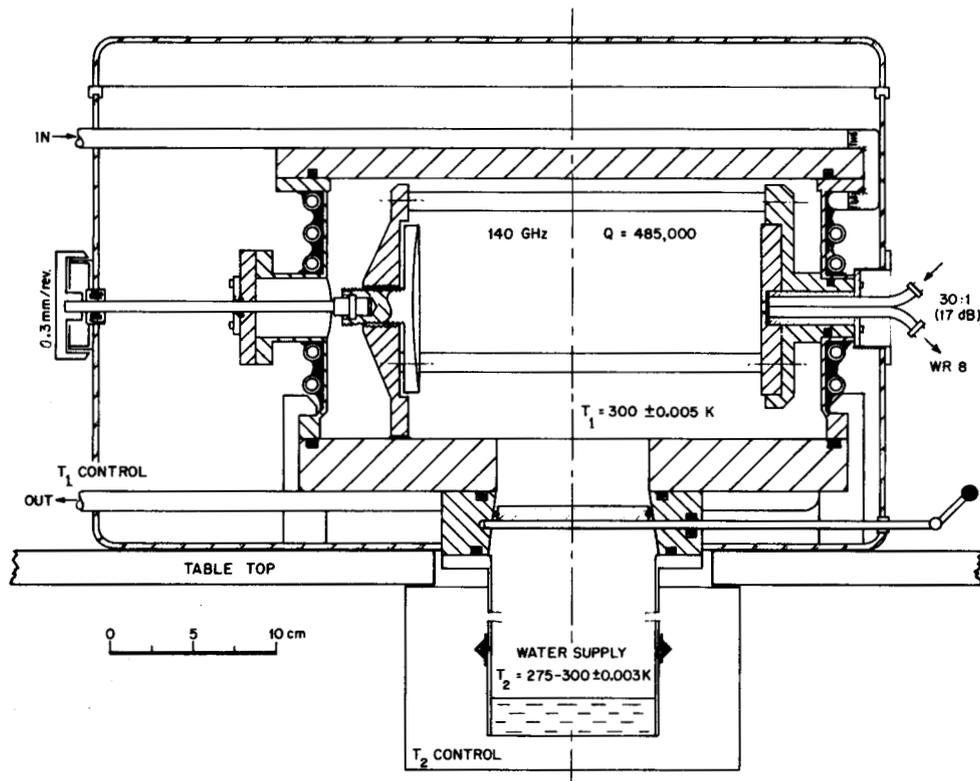


FIG. 2. Cross section of millimeter-wave spectrometer chamber with humidity simulator.⁸

graphically; results are summarized in Table I. An example is given in Fig. 3.

II. ADSORPTION THEORY

None of the coatings tested resulted in ideally hydrophobic walls, i.e., walls requiring critical supersaturation in order to form the first adsorbed layer.⁶ However, only physical adsorption (not chemical adsorption) of the water vapor was observed. All tests were in the regime of type III adsorption isotherms, according to the classification scheme of Brunauer.¹⁰ In a type III isotherm a plot of the amount of gas adsorbed versus the relative pressure (e/e_{sat}) is convex to the pressure axis. This would suggest that the attraction of ad-

sorbate molecules for each other exceeds their attraction for the adsorbent.¹¹ Such behavior would be expected for adsorbate molecules capable of strong hydrogen bonding, like water.

Because a procedure was employed that emphasized the time dependence of adsorption at saturation pressure, the entire relative pressure range of the isotherms could not be constructed. A monolayer of water is often present on surfaces exposed to water vapor, even nonporous surfaces like stainless steel. This monolayer may be chemically adsorbed, or chemisorbed, and can only be removed by evacuation at high temperatures. A monolayer of molecular water can convert a type II isotherm, which is concave to the pressure axis at low relative pressures, into a type III. Adsor-

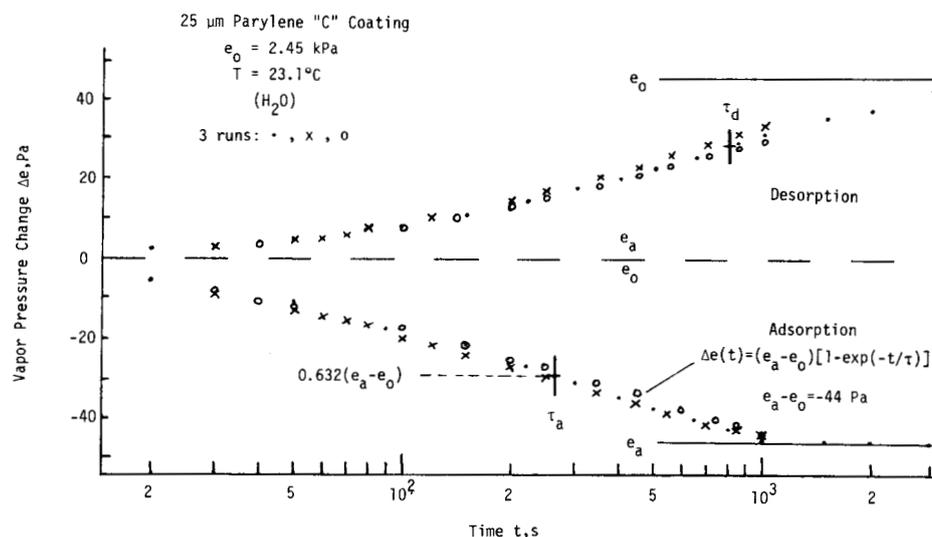


FIG. 3. Example of graphical procedure used to determine the time constants τ_a and τ_d from the beaker sorption test (see Table I).

bate-adsorbate forces will promote the adsorption of further molecules, so that the isotherm will become convex to the pressure axis.¹¹

The chemical composition of the surface of the adsorbent can cause multilayers to build up faster on some parts than on others. Adsorbate-adsorbent interaction is increased when hydroxyl groups are present on the adsorbent, as these will undergo hydrogen bonding with the adsorbate. One reason clean, polished metal surfaces are hydrophobic is because of their relative lack of sites suitable for hydrogen bonding, which compensates for their strong dispersion interactions with gas molecules. Conversely, long-chain organic polymers are desirable as hydrophobic coatings because of their weak dispersion interactions with gas molecules, despite an increased availability of possible sites for hydrogen bonding. Teflon, hexamethyldisilazane (HMDS), and parylene¹⁸ are examples of effective hydrophobic polymers.

III. COATINGS

Teflon FEP 120 (DuPont)¹⁸ is a fluorocarbon resin dispersion polymer which sticks without a primer to stainless steel. The Teflon is mixed with water and Triton X100,¹⁸ a wetting agent, prior to applications. After air drying, the Teflon is baked onto the inner surface of the test beaker. The 14-h baking process included a 30-min hold at 90 °C, a 1°C per min increase to 110 °C as a precaution against blistering by evaporating water, final heating to 360 °C, and a slow cooling down to ambient temperature. The melting point of Teflon FEP 120 is 288 °C. Table I shows that a coat of Teflon alters the hydrophobicity of clean stainless steel, the accepted standard for high vacuum work. An explanation of the sorption time behavior probably lies in the porosity of the adsorbent. Bulk polytetrafluoroethylene (DuPont PTFE Teflon),¹⁸ a material similar to FEP 120, has been found to bind more than 20 times the amount adsorbed by the surface layer of stainless steel (10.5 vs 0.5 mg/dm²).¹² The critical surface tension is an indicator of hydrophobicity towards liquid water. In this respect, PTFE (0.018 N/m) and silicone (0.020 N/m) are comparable.³

Hexamethyldisilazane is a more easily applied coating than Teflon. A small amount of HMDS (0.5 ml, or 3.95×10^{-4} ml/cm²) was injected into a beaker that was then sealed to the baseplate and allowed to stand overnight. The HMDS liquid evaporated and adhered to the cavity's interior.¹³

Parylene "C" (Union Carbide)¹⁸ is a vapor-deposited polymer (*p*-polyxylylene).¹⁴ The adhesion of parylene to stainless steel was not good, though it was improved by acid etching the surface.

Other surface treatments tested were gold plating, coating with lacquer, and coating with silicon resin. Because gold is highly resistant to oxidation, it was thought that gold plating would pacify the surface by eliminating oxidized areas that might favor water adsorption.^{15,16} Although gold plating proved a poor coating procedure in itself, perhaps a higher degree of polish would give better results.

IV. DISCUSSION

In general, desorption isotherms were found to be more reproducible and consistent than adsorption isotherms. Desorption effects were almost always slower than adsorption effects. Such hysteresis is perhaps the result of supersaturation of the condensed layer of adsorbate molecules.¹⁷

When various metal plates were coated with test substances for water drop contact angle measurements, surprisingly little correlation was found between wettability of a surface and that surface's resistance to vapor condensation. Typically, the thicker a particular coating, or combination of coatings, the more water vapor it adsorbed and the longer the time required for completed adsorption and desorption processes. A given coating might cause poor adhesion of water molecules, resulting in minimal surface migration of the molecules and, hence, hydrophobicity toward liquid water.¹⁷ Gaseous water molecules can still penetrate the coating, however; so the thicker and more porous the coating, the more water vapor it will adsorb, irrespective of the amount adsorbed on its surface. In the end, the most effective means of keeping millimeter wave-sensitive spectrometer surfaces free of condensate proved to be a slight (+ 1 °C) local heating above ambient.⁸

ACKNOWLEDGMENT

This work was supported in part by the U.S. Army Research Office under Contract No. ARO 101-83.

¹R. M. Weigand, Proc. IEEE **61**, 1167 (1973).

²R. M. Weigand, DOT Report No. FAA-RD-73-22 (AD 757744).

³J. E. Bernacki, Georgia Institute of Technology, Report No. ER-70-3, 1970.

⁴H. Hoffman, Microwave J. **22**, 43 (1979).

⁵C. A. Siller, Jr., IEEE Trans. Antennas Propag. **AP-27**, 555 (1979).

⁶H. R. Pruppacher and J. D. Klett, *Microphysics of Clouds and Precipitation* (Reidel, Boston, 1978).

⁷H. J. Liebe, Rev. Sci. Instrum. **46**, 817 (1975).

⁸H. J. Liebe, Int. J. Infrared & Millimeter Waves **5**, 207 (1984).

⁹K. T. Drzal, F. A. Putnam, and T. Fort, Jr., Rev. Sci. Instrum. **45**, 1331 (1974).

¹⁰S. Brunauer, *The Adsorption of Gases and Vapors* (Princeton University, Princeton, NJ, 1945).

¹¹S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, 2nd ed. (Academic, New York, 1982).

¹²W. Shepherd, Rev. Sci. Instrum. **44**, 234 (1973).

¹³A. L. Schmeltekopf, P. D. Goldan, W. J. Harrop, T. L. Thompson, D. L. Albritton, M. MacFarland, A. E. Sapp, and W. R. Henderson, Rev. Sci. Instrum. **47**, 1479 (1976).

¹⁴V. S. Kale, Proc. Electron. Components Conf. IEEE **28**, 344 (1978).

¹⁵J. H. Thomas, III, and S. P. Sharma, J. Vac. Sci. Technol. **13**, 549 (1976).

¹⁶S. P. Sharma and J. H. Thomas, III, J. Vac. Sci. Technol. **14**, 825 (1977).

¹⁷J. H. deBoer, *The Dynamical Character of Adsorption* (Oxford University, London, 1953).

¹⁸Certain commercial materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation, endorsement, or that the item is necessarily the best available for the purpose.