

Study of the Storage Stability of the Barium Fluoride Film Electric Hygrometer Element

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A study of the aging properties of the barium fluoride film electric hygrometer element and of possible causes of the drift of calibration with time in storage has been made. It was found that exposure of aged elements to glow discharge bombardment resulted in near recovery of the prestorage calibration, indicating that the calibration drift was not irreversible and providing insight into the mechanism of aging. Based on the likelihood that aging was due, at least in part, to contamination of the barium fluoride film, production procedures were formulated which resulted in elements with significantly reduced drift. If an adjustment is made similar to the "lock-in" procedure in the operational use of radiosonde humidity elements, then the poststorage resistance values can be adjusted to correspond closely to the prestorage calibration curves. Experimental evidence supports the hypothesis that contamination of the elements by diffusion pumping fluid in the production process was a source of the calibration drift. Applications of the element as a research tool in cloud physics, atmospheric turbulence and radio refractive index structure studies, evaporation and evaporation reduction studies, water vapor flux determinations, and tropospheric humidity distribution studies are mentioned.

Key Words: Adsorption, barium fluoride, electric hygrometer, humidity, thin films, vacuum.

1. Introduction

Possible use of the barium fluoride film electric hygrometer element [Jones, 1963; Jones, 1962a; Jones, 1962b; Jones and Wexler, 1960] on a routine operational basis has been limited by the increase in electrical resistance of the element with time in storage which results in a drift of the calibration (also referred to as "aging" of the element). It is the purpose of this paper to present results of a study of the drift problem.

The barium fluoride element, illustrated in figure 1, consists of a glass substrate on which a film of barium fluoride, 0.3μ thick, has been deposited by vapor deposition over closely spaced metallic film electrodes between which the electrical resistance can be measured or otherwise utilized in an electrical circuit. The measured resistance varies with relative humidity, RH. Laboratory determinations indicated the response time of the element to be approximately 1 sec at an ambient temperature of -20°C and 3 sec at -40°C . However, the results of field experiments, as yet unpublished, tended to show that the element was capable of more rapid response than laboratory tests have indicated. A series of radiosonde flights, previously reported [Jones, 1963], provided information on the performance of the element under conditions encountered in radiosonde flights and provided information to be used in assessing the capability of the

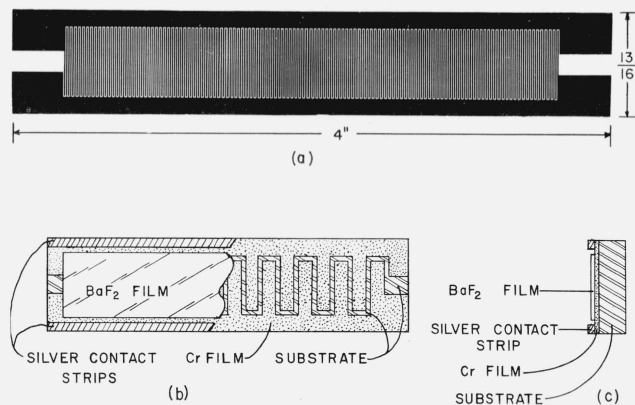


FIGURE 1. Barium fluoride film electric hygrometer element construction and electrode configuration.

element as an experimental tool for use in tropospheric humidity studies. The results for the flights corroborated laboratory test data in several areas. For example, exposure to high humidity and apparent passage through precipitation did not seem to adversely affect the functioning of the element. There was a correlation of indications of saturation or near-saturation with the presence of clouds and precipitation.

2. Glow Discharge Bombardment of Aged Elements

Elements which had been stored for approximately 6 years were recalibrated at room temperature, 23 °C. The effects of the prolonged storage on element calibration are illustrated in figure 2. It can be seen that the measured resistance had become insensitive to changes in relative humidity below about 40 percent RH and that at the higher humidities the resistance had increased by 1 to 3 orders of magnitude. The aged elements were then exposed to glow discharge in a vacuum chamber. The elements were recalibrated and the results, plotted on figure 2, indicate the effectiveness of the glow discharge procedure in accomplishing near recovery of the prestorage calibration.

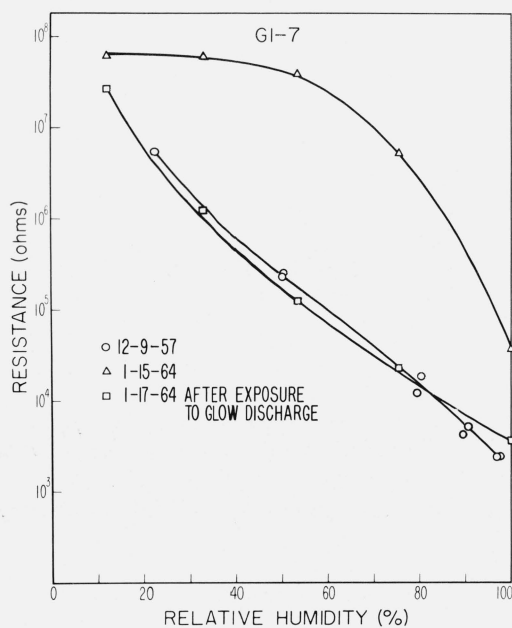


FIGURE 2. Example of the effect of long-term storage on the calibration curve and the effectiveness of the glow discharge bombardment procedure in accomplishing near recovery of the original calibration.

The apparatus, illustrated in figure 3, in which the glow discharge procedure was performed consisted of a glass bell jar evacuated by a mechanical pump and an oil diffusion pump. The pumps were fitted with liquid-nitrogen-cooled traps intended to prevent flow of oil vapors from the pumps into the bell jar. The elements were placed, with barium fluoride film side up, on a plate electrically insulated from the system. The pressure in the bell jar was reduced to, and maintained at, 80 μ of mercury by the mechanical pump. Liquid nitrogen was maintained in the mechanical pump trap. A potential difference of approximately 1,000 V dc applied between the aluminum rings produced a glow discharge which was maintained for 35 min. The current maintained by a high

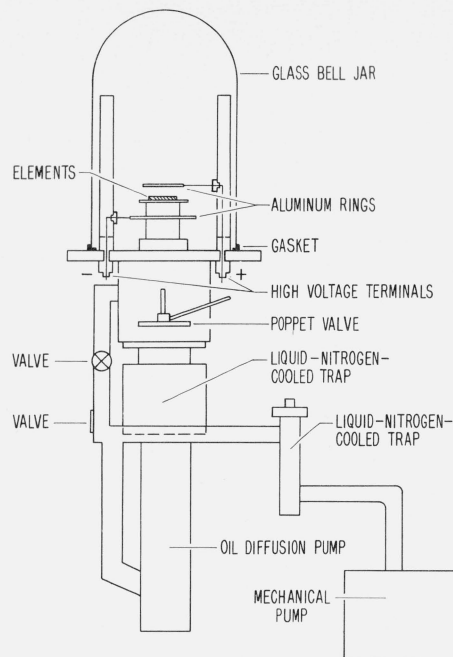


FIGURE 3. Vacuum evaporator apparatus in which the glow discharge bombardment procedure was performed.

voltage power supply was approximately 375 mA. The polarity of the aluminum ring electrodes and the location of the elements were chosen such that the elements were at least partially shielded from electron bombardment. It was assumed, therefore, that in the glow discharge the elements were bombarded by species which were predominantly positive ions.

In all cases, the glow discharge procedure was effective in reducing the resistance of the aged elements, in most cases to values near those for the original calibrations.

The outcome of the glow discharge experiment was a development of primary significance for two reasons. First, it indicated that the aging of the elements was not irreversible, at least in regard to the effects on calibration; and, second, it provided a basis for gaining insight into the mechanism of the aging process or processes. Before these points are discussed, it will be helpful to state the following *working hypotheses* concerning the functioning of the element: (1) The dominant process in the functioning of the barium fluoride film electric hygrometer element is physical adsorption of water vapor on the surface of the vacuum deposited film, of whatever composition, structure, and state of contamination. (The term "barium fluoride film" is used as a convenience and should not be construed to imply the true nature of the film.) (2) The electrical conduction process of primary interest is ionic transport in an adsorbed water film.

One can, on the basis of these hypotheses and on the basis of the glow discharge procedure results, conjecture that the aging of the elements is due, at least in part, to *contamination* of the adsorbent film by species other than water vapor. The effect of the

contaminant would be to diminish the active surface free to adsorb water vapor, therefore reducing the enhancement of conductivity attributable to the adsorbed water film. The effect of the ion bombardment of aged elements in the glow discharge could then be to provide active surface free (or relatively so) of contaminants (or of a specific contaminant).

A possible source of contamination of the elements is backstreaming oil vapors from the mechanical pump and the oil diffusion pump into the vacuum chamber in which the barium fluoride films were deposited. Holland and others [Holland, 1963; Holland and Bateman, 1961; Holland, 1960; Holland and Bateman, 1960; Holland, 1958; Bateson, 1952] have investigated the sources of surface contamination in vacuum evaporation systems. The following points summarized from the published accounts of their investigations are considered to be pertinent to the present discussion. (1) A chemically clean surface exposed in a vacuum system evacuated by oil diffusion pumps and/or sealed by Neoprene gaskets becomes partially covered by a physically adsorbed layer in equilibrium with organic vapors. (2) A highly reactive surface, created "in vacuo" by fracturing glass or depositing a silica film from the vapor phase, rapidly chemisorbs contaminants. (3) If a freshly deposited silica film is held at a temperature of about 200 °C in the presence of vapor from a silicone pumping fluid, a silicone film is chemisorbed at a greatly reduced rate. (4) *Electron* bombardment in hydrocarbon vapors produces hydrophobic films; electron bombardment in silicone vapors forms hydrophilic polymerized films. (5) A fluorinated hydrocarbon, Viton, and a silicone diffusion pumping fluid with an exceptionally low vapor pressure, DC705, help to decrease the partial pressure of organic contaminants in a vacuum atmosphere but do not completely eliminate possible surface contamination. (6) Holland has devised a glow discharge cleaning apparatus in which the cathode electrode is shielded and in the application of which it is claimed that the glass surface is exposed to the plasma or positive column only of the discharge. (7) A clean surface attained in glow discharge can become contaminated if organic molecules are present in the vacuum atmosphere. Therefore, the time interval between glow discharge cleaning and reducing of pressure to that for evaporation must be kept to a minimum to avoid substrate contamination.

The vacuum evaporator in which the barium fluoride films have been deposited is evacuated by a mechanical pump and an oil diffusion pump. Initially, the fluid in the diffusion pump was Octoil (di-2-ethyl hexyl phthalate). Subsequently, Octoil S (di-2-ethyl hexyl sebacate) was used, which, in turn, was replaced by DC704 silicone and then by DC705 silicone. The original bell jar gasket material was Neoprene. Subsequently, this was replaced by Viton. The cathode in the glow discharge apparatus originally was not shielded effectively and, therefore, bombardment of substrates by electrons probably occurred. In the early

work on the barium fluoride element, the pumps had not been fitted with liquid-nitrogen-cooled traps. The efficiencies of the traps, installed for later work, in preventing the backstreaming of oil vapors into the vacuum chamber are not known. It is evident, therefore, that sources of contamination in the vacuum evaporation system of the sorts investigated by Holland and others can be considered to have been present in some degree throughout the previous barium fluoride film work.

3. Production of Elements of Reduced Calibration Drift

In consideration of the arguments in the preceding section, the procedures for the production of barium fluoride elements were modified in the following respects:

(1) In the final cleaning in the vacuum chamber, the glass substrates were shielded from direct electron bombardment from the negative glow discharge electrode.

(2) After the barium fluoride film was deposited, the elements were subjected to glow discharge before they were exposed to the ambient atmosphere. For the post-deposition bombardment, liquid nitrogen was maintained in the mechanical pump trap.

Using the modified procedures, elements were produced and stored in sealed containers over a desiccant, barium oxide (BaO), from which they were occasionally removed for room temperature calibration.

The data for repeated calibrations of a typical element produced by the modified procedures are plotted in figure 4. It can be seen that, in general, the resist-

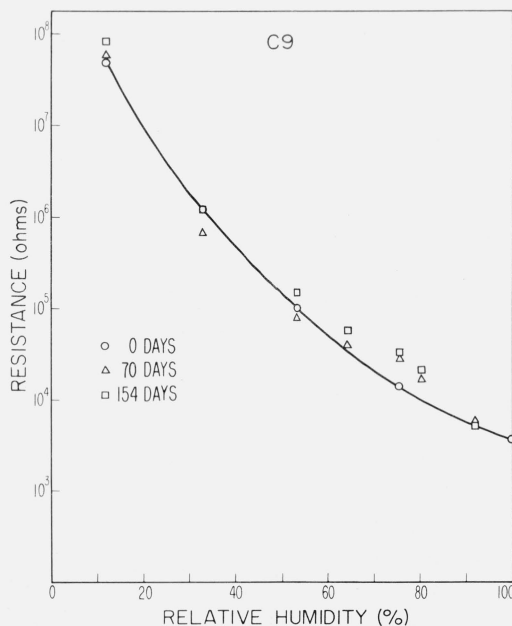


FIGURE 4. Example of the effect of storage on the calibration of elements produced by procedures in which the substrate and the finished element were subjected to glow discharge bombardment.

ance of the element had increased in storage over BaO. However, the increase in resistance is significantly smaller than that for elements produced by the conventional procedures.

As an indicator of the effect of storage on the calibration of the elements, the ratio of the resistance after storage, R , to that before storage, R_0 , is tabulated in table 1. Maximum, minimum, and arithmetic mean values of R/R_0 throughout the room temperature humidity range, 12 percent to 92 percent RH, have been tabulated for storage periods of various lengths.

TABLE 1. Resistance ratios, R/R_0 , after storage over barium oxide

Element	Max ¹	Min ²	Mean	Max ¹	Min ²	Mean	Max ¹	Min ²	Mean
	27 Days			70-75 Days			154-157 Days		
C1	5.1	1.4	3.0	4.3	1.7	2.6	3.9	1.7	2.9
C2	1.9	1.3	1.6	3.1	1.2	1.3	2.2	1.4	1.9
C3	2.1	1.2	1.6	1.7	0.80	1.2	1.6	1.5	1.5
C4	2.7	1.4	1.9	2.0	.79	1.2	3.1	1.0	1.8
C5				1.7	.54	1.1	2.0	0.76	1.3
C6				1.3	.89	1.1	3.5	1.5	2.4
C7				1.1	.93	1.0	2.6	1.2	2.0
C9				2.0	.58	1.3	2.4	1.0	1.6
C10				1.7	.61	1.2	2.4	1.3	1.8
C11				2.0	.83	1.4	2.6	1.6	2.1
C12				3.7	.59	1.8	6.0	1.7	3.3
	139-140 Days			228 Days			248 Days		
S1	1.7	1.5	1.6	2.1	0.70	1.5			
S2	2.9	1.8	2.3	3.4	.90	2.4	3.9	1.9	3.0
S3	4.9	1.8	3.2	4.6	.65	3.1	5.6	1.1	4.3

¹ Maximum value of R/R_0 .
² Minimum value of R/R_0 .

Elements C1 through C4 were produced in the same deposition; C1 and C2 were removed from the vacuum chamber before C3 and C4 were subjected to the post-deposition bombardment and, thus, were not subjected to the post-deposition bombardment. Elements C5 through C12 were produced in a single deposition. Elements S1 through S3 were produced by depositing the barium fluoride film over Nichrome V metallic film electrode configurations provided by a commercial source.

The deviations, in percent RH, of the post-storage calibration points from curves drawn through the prestorage calibration points are tabulated in table 2. The deviations are predominantly of negative sign, indicating that resistance had increased in storage. The arithmetic means of the absolute values of deviations corresponding to a storage period of approximately 5 months for elements C3 through C12 (elements which had been subjected to the post-deposition bombardment) range from 2.9 to 9.2 percent RH. The arithmetic means of the absolute values of deviations corresponding to a storage period of 7½ months for the S-series elements range from 5.8 to 9.8 percent RH.

The post-storage resistance values obtained for the individual elements were adjusted by multiplication by the inverse of the arithmetic mean values of the resistance ratio, R/R_0 , for the individual elements. The effect of this operation, which is related to the "lock-in" procedure in the operational use of radio-sonde humidity elements, is to bring the post-storage humidity indications into the vicinity of the pre-storage calibration curves. The deviations in percent RH, of the adjusted resistance values about the arbi-

TABLE 2. Deviations (in % RH) of the indications for stored elements from curves drawn through the prestorage calibration points.

Results for 12%, 33%, 53.5%, 75.5%, and 92% relative humidity points only have been included.

Element	Max ¹	Min ²	(-) ³	(+) ⁴	$\overline{ d }$ ⁵	Max ¹	Min ²	(-) ³	(+) ⁴	$\overline{ d }$ ⁵	Max ¹	Min ²	(-) ³	(+) ⁴	$\overline{ d }$ ⁵
C1	-3.0	-10.5	4	0	6.1	-2.0	-11.5	5	0	6.5	-3.0	-15.5	4	0	9.4
C2	-3.0	-4.5	4	0	3.8	-1.5	-6.0	5	0	3.5	-2.5	-9.5	5	0	7.1
C3	-1.0	-5.0	4	0	2.9	+2.0	-3.5	3	2	2.1	-1.5	-8.5	5	0	4.7
C4	-2.0	-7.0	4	0	4.4	+3.0	-2.5	1	3	1.8	0.0	-7.5	4	0	3.8
C5						+1.0	-8.0	4	1	4.7	-1.0	-8.0	5	0	2.9
C6						+0.5	-2.5	2	1	0.7	-1.0	-10.0	3	0	4.2
C7						+0.5	-1.0	2	1	0.4	-2.5	-10.0	4	0	6.2
C9						+4.5	-8.5	3	2	4.3	0.0	-10.5	4	0	4.1
C10						+3.0	-7.0	3	2	3.3	-2.0	-11.5	5	0	5.4
C11						+1.5	-8.5	3	1	3.8	-1.5	-12.0	5	0	6.6
C12						+3.5	-13.0	4	1	5.5	-3.0	-18.0	5	0	9.2
	139-140 Days			228 Days			248 Days								
S1	+1.0	-8.5	3	1	4.1	+5.5	-10.0	3	1	5.8					
S2	-5.0	-9.5	4	0	7.2	+1.0	-11.5	3	1	7.2	-5.0	-13.0	4	0	9.4
S3	-5.0	-14.5	4	0	9.8	+2.5	-16.0	3	1	9.8	-1.0	-20.0	4	0	12

¹ Most positive or least negative deviation.
² Most negative deviation.
³ Number of negative deviations.
⁴ Number of positive deviations.
⁵ Arithmetic mean of the absolute values of the deviations.

rary curves drawn through the pre-storage data are tabulated in table 3. The arithmetic mean of the absolute values of the deviations ranges from 0.3 to 4.6 percent RH, with values of 2.5 and 2.8 percent RH for the two elements stored for 248 days.

The following conclusions can be drawn from the data for the elements produced by the modified procedures:

(a) The modified procedures resulted in the production of elements which were more stable, i.e., elements with reduced drift of calibration in storage

(b) The adjustment operation was effective in providing a correction for aged element resistance values to provide a calibration in the vicinity of the prestorage calibration curves. This result implies that the shift of calibration to higher resistances with time in storage

TABLE 3. Deviations (in % RH) of the indications for stored elements, adjusted by multiplying the resistance values by the inverses of the appropriate mean resistance ratios, from curves drawn through the prestorage calibration points

Element	Max ¹	Min ²	(-) ³	(+) ⁴	$\overline{ d }$ ⁵	Max ¹	Min ²	(-) ³	(+) ⁴	$\overline{ d }$ ⁵	Max ¹	Min ²	(-) ³	(+) ⁴	$\overline{ d }$ ⁵
	27 Days					70-75 Days					154-157 Days				
C1	+1.0	-1.5	1	1	0.8	+3.5	-2.0	1	4	1.8	+4.0	-3.0	2	2	2.3
C2	+2.5	-1.0	2	1	1.0	+1.0	-5.0	2	2	1.8	+2.5	-7.0	4	1	2.5
C3	+4.5	-5.5	1	2	2.2	+3.5	-3.0	3	2	2.2	0.0	-1.0	2	0	0.3
C4	+1.5	-3.5	1	2	1.5	+3.5	-2.0	1	4	3.3	+4.5	-2.0	1	3	2.0
C5						+6.0	-6.5	3	2	3.8	+4.0	-4.0	2	3	3.0
C6						+1.5	-2.0	1	3	0.9	+4.5	-4.0	2	2	2.5
C7						+0.5	-0.5	2	1	0.3	+0.5	-2.5	3	1	1.2
C9						+6.0	-6.0	2	3	4.1	+3.5	-5.5	1	2	1.9
C10						+4.0	-5.0	2	2	3.1	+2.0	-4.5	2	3	1.8
C11						+3.5	-4.5	2	3	2.7	+1.0	-3.5	2	2	1.4
C12						+7.5	-7.5	2	3	4.6	+4.5	-6.5	3	2	3.5
	139-140 Days					228 Days					248 Days				
S1	+0.5	-2.5	1	1	0.8	+3.5	-5.5	2	2	3.5					
S2	+2.0	-1.5	1	3	1.4	+7.0	-3.0	2	2	3.0	+3.5	-3.0	2	2	2.5
S3	+3.5	-1.5	1	3	2.5	+7.0	-4.0	2	1	3.6	+6.0	-2.0	2	1	2.8

¹ Most positive or least negative deviation.

² Most negative deviation.

³ Number of negative deviations.

⁴ Number of positive deviations.

⁵ Arithmetic mean of the absolute values of the deviations.

is not, in general, accompanied by a significant change in the *shape* of the calibration curve. From a practical point of view, it would be possible to use the original calibration curves with aged elements, the post-storage resistance values of which had been adjusted.

4. Investigation of a Diffusion Pumping Fluid as a Possible Source of Calibration Drift

The effectiveness of the modified procedures in producing more stable elements is thought to be due to the reduction of contamination of the elements. If a source of contamination is pumping fluid vapor in the vacuum evaporator, as appears probable from the discussion of section 2, then shielding of the substrates from direct electron bombardment from the negative glow discharge electrode would be expected to have reduced the amount of material deposited by electron bombardment in the presence of pumping fluid vapors (item 4 of section 2). The post-deposition bombardment could have removed physically adsorbed organic vapors (item 1 of section 2) from the barium fluoride film. The liquid-nitrogen-cooled mechanical pump trap served to reduce the backstreaming of oil

vapor from the mechanical pump into the vacuum chamber during the post-deposition bombardment. The data does not, however, show a statistically significant difference between elements produced with and without the post-deposition bombardment.

On the basis of these results, several experiments were performed to test the hypothesis that contamination by diffusion pumping fluid is a source of the drift of the calibration of the barium fluoride element. These experiments were patterned after similar experiments reported by Holland (1963).

Barium fluoride elements were produced by the deposition of the barium fluoride film on a substrate which had been exposed to the negative glow discharge electrode, and which was presumed therefore to have been bombarded by electrons in the glow discharge prior to the deposition of the barium fluoride film. The resistance of the element was measured at various times at room temperature at 33 percent RH (considered to be an optimum value of RH for detection of calibration shift) during storage over BaO. In figure 5, the resistance ratio, R/R_0 , and the logarithm of R/R_0 , at 33 percent RH are plotted against time in storage for a typical element, C38.

Another set of elements was produced by the deposition of barium fluoride on substrates which had

been exposed to the negative electrode in glow discharge; dishes containing a diffusion pumping fluid, Octoil S, had been placed in the vacuum chamber and remained there during the bombardment and during the deposition of the film. Results of resistance measurements for a typical element, C43, at 33 percent RH during storage over BaO are plotted in figure 5. The curve designated CR500F applies to an element which exhibited exaggerated drift and was included in figure 5 for comparison purposes.

As can be seen in figure 5, both sets of elements, produced on electron-bombarded substrates, increased in resistance at 33 percent RH during storage over BaO. Over the time period studied, the increase in resistance was greater for the elements produced in the presence of the intentionally introduced pumping fluid vapor.

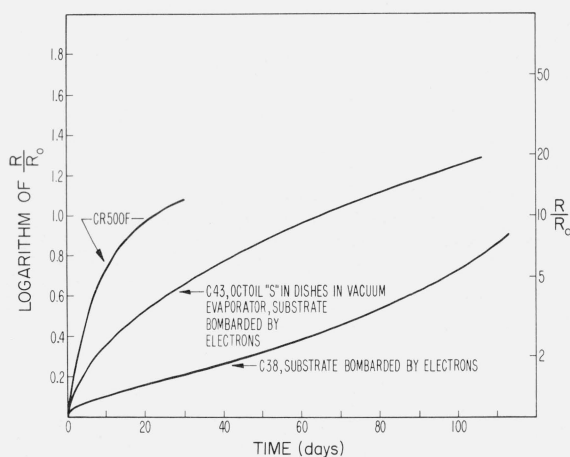


FIGURE 5. Example of the effects of storage over BaO on the resistance ratio at 33 percent RH for elements for which the substrates had been exposed to electron bombardment, in the absence and presence of Octoil S in the vacuum chamber.

Another set of elements was produced on substrates which were shielded from direct electron bombardment in the predeposition glow discharge and in a post-deposition bombardment. After subsequent room temperature calibration, the elements were returned to the vacuum evaporator and exposed to a dish containing Octoil S. Spots appeared on the film, presumably due to bursting of bubbles which formed in the oil at the reduced pressure. The resistance ratio for a typical element, C33, was found to be 13. The elements were then degreased in a vapor degreaser in which the solvent was isopropyl alcohol. Spots were no longer visible to the unaided eye and R/R_0 decreased to 1.9. The elements were returned to the vacuum chamber and exposed to a dish containing Octoil S; a shutter placed above the surface of the oil prevented the formation of spots on the film. R/R_0 at 33 percent RH was 8.7 after this second exposure to Octoil S. After storage overnight over BaO, after which R/R_0 at 33 percent RH was 4.8, the elements

were degreased and then exposed to glow discharge, shielded from direct electron bombardment, in the vacuum chamber. R/R_0 at 33 percent RH was 3.1 after the bombardment. The elements were then stored in a sealed container over BaO for 109 days. R/R_0 at 33 percent RH increased to a value of 83 at the end of the storage period. These results are plotted in figure 6. The numbers on the circles indicate the sequence of events.

The results plotted in figure 6 can be interpreted in the following way. The rise in R/R_0 after exposure to Octoil S in the vacuum evaporator can be attributed to contamination of the barium fluoride film by liquid oil and oil vapor, resulting in a loss of surface available for the adsorption of water vapor. The subsequent degreasing removed part of the oil contaminant, uncovering relatively active surface for the adsorption of water vapor and the resistance ratio consequently decreased. The second exposure to Octoil S contaminated the surface again with adsorbed vapor and, consequently, the resistance ratio increased to a value somewhat less than that in the presence of spots on the surface. Vapor degreasing and bombardment removed part of the contaminant and subsequent storage over BaO resulted in increasing R/R_0 throughout the 109-day storage period, perhaps due to the diffusion of the contaminant to an increasingly large area of the active surface.

The results of these experiments, although not definitive, are consistent with the hypothesis that contamination by diffusion pumping fluid is a source of the drift of the calibration of the barium fluoride element.

5. Effects of Repeated Bombardment and Prolonged Bombardment on Calibrations for Aged Elements

Returning now to the effects of glow discharge bombardment on the calibration of elements which

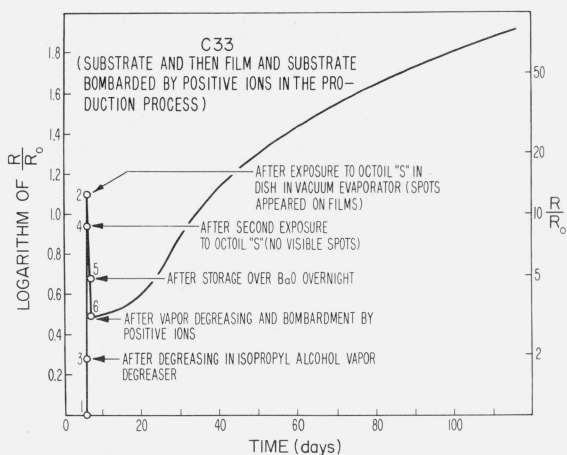


FIGURE 6. Example of the results for an experiment designed to investigate the effects of Octoil S contamination on resistance ratio at 33 percent RH.

had been stored for 6 years, it was observed that a second bombardment after an intervening period of approximately 5 months of storage over BaO (during which time the resistance had increased) resulted in a shift in calibration to resistances lower than those for the original prestorage calibration. This significant result will be discussed later. The calibration curve after the second bombardment is shown in figure 7.

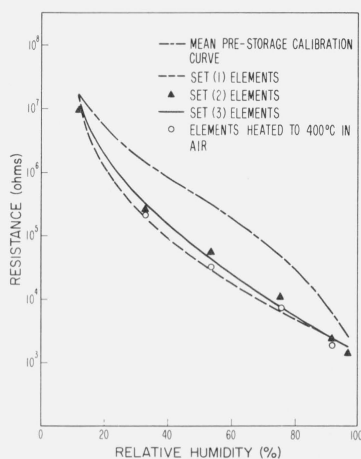


FIGURE 7. Plots of calibration data for three sets of elements: (1) aged elements exposed to a second glow discharge, (2) aged elements exposed to glow discharge for 8 hours, and (3) elements produced by procedures modified to minimize contamination. The mean prestorage curve and data for elements heated to 400°C in air are shown for comparison.

In consideration of the possibility of diffusion of contaminants on the elements, other elements which had been stored for at least 6 years were subjected to prolonged glow discharge bombardment for periods as long as 8 hr. The elements were placed on a plate over the diffusion pump port and were bombarded using aluminum electrodes in an assembly similar to that described by Holland (1958, 1961). In this assembly the negative electrode is shielded and it is therefore assumed that the elements were exposed to positive species of the discharge. The power in the glow discharge was adjusted to attain and maintain a temperature on the elements of approximately 150°C. The elevated temperature was expected to facilitate diffusion. The geometric mean of the measured resistances for 11 elements at each RH for the post-bombardment calibration are plotted in figure 7. These values were found to be lower than the corresponding values for the typical prestorage calibration curve also shown in the figure 7. After 10 days in storage over BaO, the calibration curve had shifted significantly toward higher resistances. Also, an apparent hysteresis effect was observed when the resistance was measured at 33 percent RH, then at 97 percent RH, and again at 33 percent RH. The second measurement at 33 percent RH was found to be lower than the first by a factor of approximately 4. These results will be discussed in a later section.

6. Modification of Production Procedures to Minimize Possibility of Contamination of Elements

On the basis of the results of various experiments in this work and the considerations concerning the possibility that contamination by diffusion pumping fluid is a source of the drift of the calibration of the barium fluoride element, the procedures for the production of barium fluoride elements were again modified as follows:

(1) Liquid nitrogen was maintained in both the mechanical pump cold trap and the oil diffusion pump trap throughout the production process.

(2) The distance between the evaporation (barium fluoride) source and the substrates was reduced from 38 cm to 19 cm.

(3) The substrates were exposed to a glow discharge for approximately 76 min during which time the substrate temperature increased to approximately 160°C. The glow discharge was produced by the electrode assembly used for the prolonged glow discharge exposure of aged elements in section 5, presumably exposing the substrates to positive species in the discharge, and reducing if not eliminating electron bombardment.

(4) The deposition of the barium fluoride was started within 3 min after the glow discharge power supply had been turned off. The substrate temperature during the deposition was, therefore, near 160°C.

(5) The time of deposition was reduced from 300 sec to 180 sec.

(6) Argon was introduced into the evaporator as soon as practicable after the deposition of the film to bring the pressure to ambient in the relative absence of oxygen.

(7) The elements were not subjected to a post-deposition glow discharge bombardment.

It should be noted that the pumping fluid in the diffusion pump was DC705 silicone and the bell jar gasket was made of Viton.

These procedures permitted the deposition of the barium fluoride film on substrates which had been bombarded by positive (assumed) ions for a relatively extended period of time and on which the temperature was maintained at about 160°C to inhibit sorption of silicone vapor and other vapors present in the vacuum evaporator, with a minimum of time during which the substrates and film might be exposed to contaminants in the vacuum evaporator, and with cooling of the elements in a relatively inert atmosphere during the return to ambient pressure.

A room temperature calibration curve for elements produced under these modified procedures is plotted in figure 7. The curve was drawn through points representing the geometric mean of the resistances for 4 elements at each RH point. It can be seen that this curve falls below (in resistance) the mean curve for elements produced by the conventional procedures.

On examination of figure 7, the similarity in shape of calibration curves for three sets of elements: (1) the set of aged elements which were exposed to a second glow discharge bombardment, (2) the set of aged elements which were exposed to glow discharge bombardment for 8 hr, and (3) the set of elements produced by the modified procedures of this section, is conspicuous. Also, the fit of the points for set (2) to the curve for set (3) is good. These results are especially significant considering the large displacements of the data for these sets of elements from the mean calibration curve for elements produced by the conventional procedures. It is, therefore, reasonable to inquire as to what these three sets of elements had in common. On the basis of the hypothesis that contamination of the barium fluoride elements by diffusion pumping fluid (and other contaminants) is a source of the drift of the calibration of the elements, one possible answer to the question is the conjecture that the surfaces of the three sets of elements were relatively free of contamination. It is to be recalled that the apparent effect of glow discharge exposure of aged elements was to essentially (and temporarily) reverse the effect of aging on the calibration of the elements. On the basis of the working hypotheses stated in section 2 it was conjectured that the effect of the glow discharge exposure could be to provide active surface free (or relatively so) of contaminants (or of a specific contaminant). Therefore, it can be conjectured that the second glow discharge bombardment and the 8-hr glow discharge bombardment were more efficient in providing active surface free of contaminants than was a single exposure to bombardment, thereby accounting for the lower resistances for sets (1) and (2) compared with prestorage values. Also, the modified procedures under which set (3) elements were produced were specifically formulated to minimize contamination of substrates and elements. Again, this could account for the lower resistances for set (3) elements. That the calibration curves for the three sets of elements should be similar in shape and relatively close together on figure 7, is, therefore, a not unexpected result. It is interesting to note that the open circles, corresponding to room temperature calibration points for elements which, in earlier work [Jones and Wexler, 1960], had been heated to 400 °C in air in a muffle furnace, fit the curve for set (1) elements over the range 33 percent to 92 percent RH.

The apparent hysteresis phenomenon observed for set (2) elements was also observed for set (3) elements. It is not known whether such a phenomenon existed for set (1) elements. The investigation of this and other properties of set (3) elements is continuing, and therefore, the results presented here for these elements must be considered to be preliminary.

It seems appropriate at this point to make some remarks regarding hysteresis in physical adsorption systems, since it has been hypothesized (working hypothesis 1 in section 2) that the dominant process in the functioning of the barium fluoride film electric hygrometer element is physical adsorption. Hysteresis, both reversible and irreversible, in the physical ad-

sorption process has been studied by many investigators and several theories have been advanced. Hysteresis is said to be reversible if the adsorption isotherm is completely reproduced on repetition of the adsorption-desorption cycle and is said to be irreversible if repetition of the cycle results in a different curve [Brunauer, 1945]. In the case of the barium fluoride element, for which the calibration curve can be considered to be related to an adsorption isotherm [Jones, 1962a], the hysteresis has been found to be irreversible. Brunauer asserts that according to Zsigmondy's (1911) view hysteresis is not a property of the adsorbing system but is due to an extraneous effect, impurities, and that the desorption branch represents adsorption on an adsorbent from which impurities have been removed and therefore is the true equilibrium curve. It is not asserted here that Zsigmondy's theory best accounts for hysteresis, but rather only that the results in the present work fit into this theory rather well. The relatively large hysteresis effect observed for elements with presumably more active surfaces (i.e., elements of sets (2) and (3)) might be attributable to higher sensitivity of these more active surfaces to contamination by components of laboratory air at low relative humidity.

7. The Element as a Research Tool

Although possible use on a routine basis has been limited by aging of the element, a situation which the results of the present work substantially relieves, the element has shown promise for immediate use as a research tool. Such application has been made in the following areas, the results for which are as yet unpublished:

(1) Aircraft cloud physics studies. Thirteen flights of elements mounted on the exterior fuselage of an aircraft have been made.

(2) Atmospheric turbulence and radio refractive index structure studies.

(3) Studies of evaporation and evaporation reduction from a fresh water lake.

(4) Determination of water vapor flux from natural surfaces. Preliminary studies of the applicability of the element have been made and, at this writing, application in a micrometeorological field experiment is imminent.

(5) Tropospheric humidity distribution studies. In addition to the series of radiosonde flights mentioned above [Jones, 1963], an element provided the only tropospheric humidity measurements on a manned balloon flight.

In all of these areas the results have been encouraging.

8. Conclusions

(1) The work reported here has substantially improved the storage stability of the barium fluoride film electric hygrometer element.

(2) The potential of the element as a research tool, primarily due to its rapid response, has begun to be realized in several fields.

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