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**Evaluation of Liquid-Gas Separator
Materials for a Silver Zinc Cell Vent**

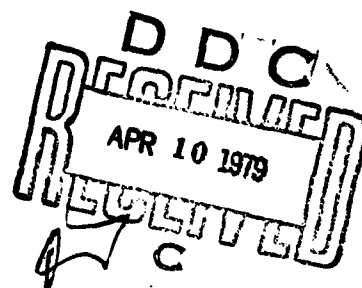
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Final Report

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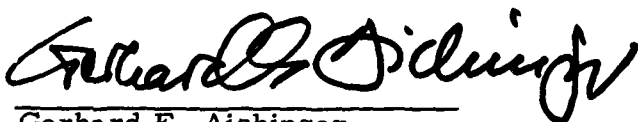
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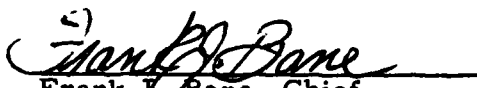
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Project Officer

FOR THE COMMANDER



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EVALUATION OF LIQUID-GAS SEPARATOR MATERIALS FOR A SILVER ZINC CELL VENT

A. INTRODUCTION

The efficient operation of vented battery cells in an aerospace environment is dependent upon proper venting of gases and negligible loss of electrolyte. In silver zinc battery cells, hydrogen is slowly released as a result of zinc corrosion, and oxygen may be evolved from adsorbed gases or Ag_2O decomposition at higher temperatures. The liquid-gas separator that is typically used to vent these gases is generally a porous material or a semipermeable membrane. These materials, to be effective, must be highly permeable to gas but essentially impermeable to electrolyte. Some silver zinc battery cells use a sintered Teflon disc liquid-gas separator. Although it has adequate gas permeability, this separator does allow electrolyte to escape from the cell under conditions of electrolyte contact, such as from foaming. Another separator that has been successfully used in silver zinc cells consists of a semipermeable polyethylene membrane.¹ This report gives the results of tests relating to gas and electrolyte permeabilities for a number of potential separator materials.

B. SEPARATOR REQUIREMENTS

The permeability requirements for the liquid-gas separator may be estimated from the battery temperature requirements, the maximum allowed gassing rate, and the maximum allowed internal cell pressure for battery operation. The maximum required gas permeability is estimated to be $36 \text{ cm}^3/\text{min}$ for H_2 and $3.6 \text{ cm}^3/\text{min}$ for O_2 at a 15-psi pressure differential and 110°F for a particular battery cell. These rates are twice those computed from the maximum allowed gassing rate of $1.0 \text{ cm}^3/\text{min}$ at 70°F , and from the temperature dependence of the gassing rate. The 110°F

¹T. J. Hennigan and C. F. Palandati, Zinc-Silver Oxide Batteries, ed. A. Fleischer and J. J. Lander, John Wiley and Sons, Inc., New York (1968), Chap. 31, p. 436.

temperature is specified because the separator permeability will be at its minimum at the upper temperature extreme (due to the increased gas viscosity) where the rate of gas evolution is highest. The separator is therefore expected to exceed these specifications at the lower temperatures. An electrolyte permeability of 0.05 g/day is arbitrarily chosen as an upper limit so that little electrolyte will be lost during the useful lifetime of the battery cell. Therefore, an electrolyte permeability less than this value is desired. The electrolyte permeability specification is for ZnO-saturated KOH electrolyte (specific gravity 1.35), whereas the gas permeability specification is for gas saturated with this electrolyte. The separator must also be designed to rupture if the internal cell pressure exceeds approximately 22 psi. This prevents the cell casing from being ruptured by excessive buildup of internal pressure. This rupturing of the separator may be irreversible.

C. MATERIALS

The materials that were given preliminary tests for gas permeability were 1 mil FEP Teflon, 3 mil TFE Teflon, 1 mil polyethylene, and 17.5 mil microporous Teflon. The FEP and TFE Teflon were obtained from Industrial Plastic Supply, Inc., the polyethylene was obtained from a standard protective dry cleaning bag, and the microporous Teflon was supplied by Curtis Brown of Eagle Picher Industries. Of these four materials, only the microporous Teflon had sufficient gas permeability at room temperature; therefore, the other materials were not tested further. The gas and electrolyte permeabilities of microporous Teflon were then measured at various temperatures to evaluate the usefulness of this material as a separator.

D. PERMEABILITY TESTS

The gas and electrolyte permeability tests were conducted using the apparatus illustrated in Figure 1. The separator holder was constructed of plexiglass with stainless steel fittings. All gas permeability measurements were done after bubbling the gas through a ZnO-saturated KOH

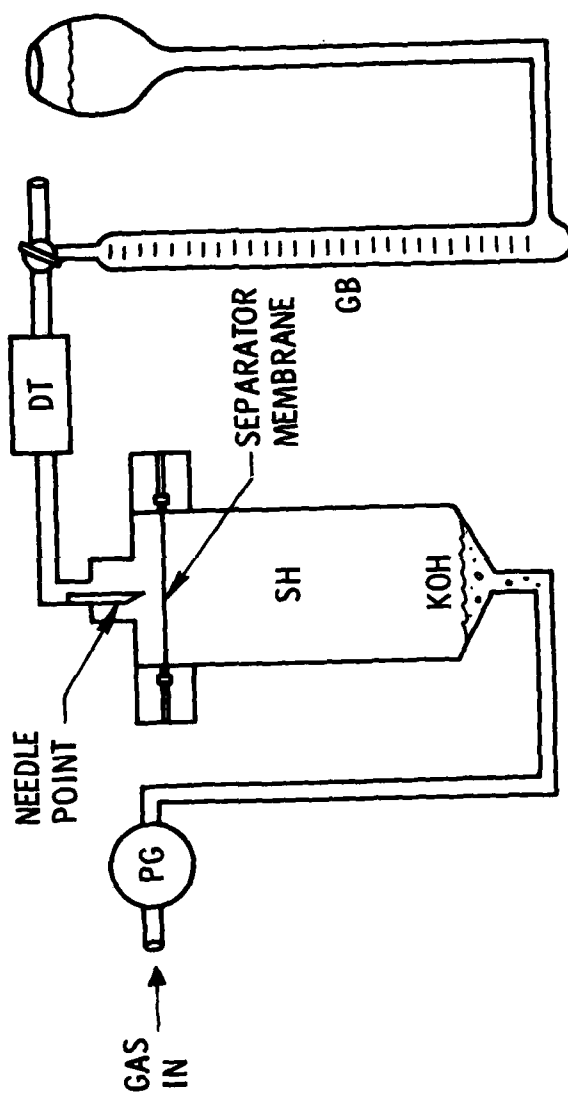


Figure 1. Apparatus used for measuring gas and electrolyte permeability of separator materials. PG is a pressure gauge; SH is the separator holder; the needle point is for puncturing the separator at a given limit of distension; DT is a drying tube for absorbing water or electrolyte passed through the separator; and GB is a gas burette.

electrolyte reservoir in the bottom of the apparatus. The permeabilities of microporous Teflon to H_2 and O_2 are presented in Figures 2 and 3, respectively. A separator disc with a 2.5-cm^2 area was used for the tests. For H_2 the flow rate increases with pressure in a quadratic fashion up to about 5 psi, but above this pressure increases more or less linearly exhibits a sharp increase between 4 and 5 psi. The sharp increase is likely exhibits a sharp increase between 4 and 5 psi. The sharp increase is likely to be the result of the transition from viscous flow at low pressures to turbulent flow at higher pressures. Theoretical considerations² predict a quadratic increase in flow rate with pressure in the regime of viscous flow, a prediction that is in agreement with the low pressure flow rate shown in Figure 2. The O_2 flow rate, which is indicated in Figure 3, has a somewhat linear dependence on pressure over the entire pressure range from 3 to 15 psi, although there is an indication of quadratic behavior at very low pressures. To verify that the flow regime observed for oxygen is the same as that observed for H_2 at higher pressures, we plotted the ratio of the flow rates for H_2 and O_2 as a function of pressure (Figure 2). In the same flow regime, this ratio should be 4 (the square root of the mass ratio of O_2 to H_2). Figure 2 indicates this ratio to be about 3.6 after H_2 attains turbulent flow. Thus O_2 exhibits turbulent flow at quite low pressures relative to H_2 , a result that is reasonable since the type of flow regime, or Reynolds number,² is proportional to gas density. For both gases, turbulent flow is achieved at relatively low pressures because of the complex, sponge-like pore structure of the microporous Teflon.

The dependence of the H_2 flow rate on temperature T is indicated in Figure 4. As expected, the flow rate decreases with increasing temperature since the gas viscosity increases with temperature. If viscosity changes account for the entire temperature dependence, a plot of flow rate as a

²H. Melville and B. G. Gowenlock, Experimental Methods in Gas Reactions, MacMillan and Co. Ltd., New York (1964), pp. 22-23.

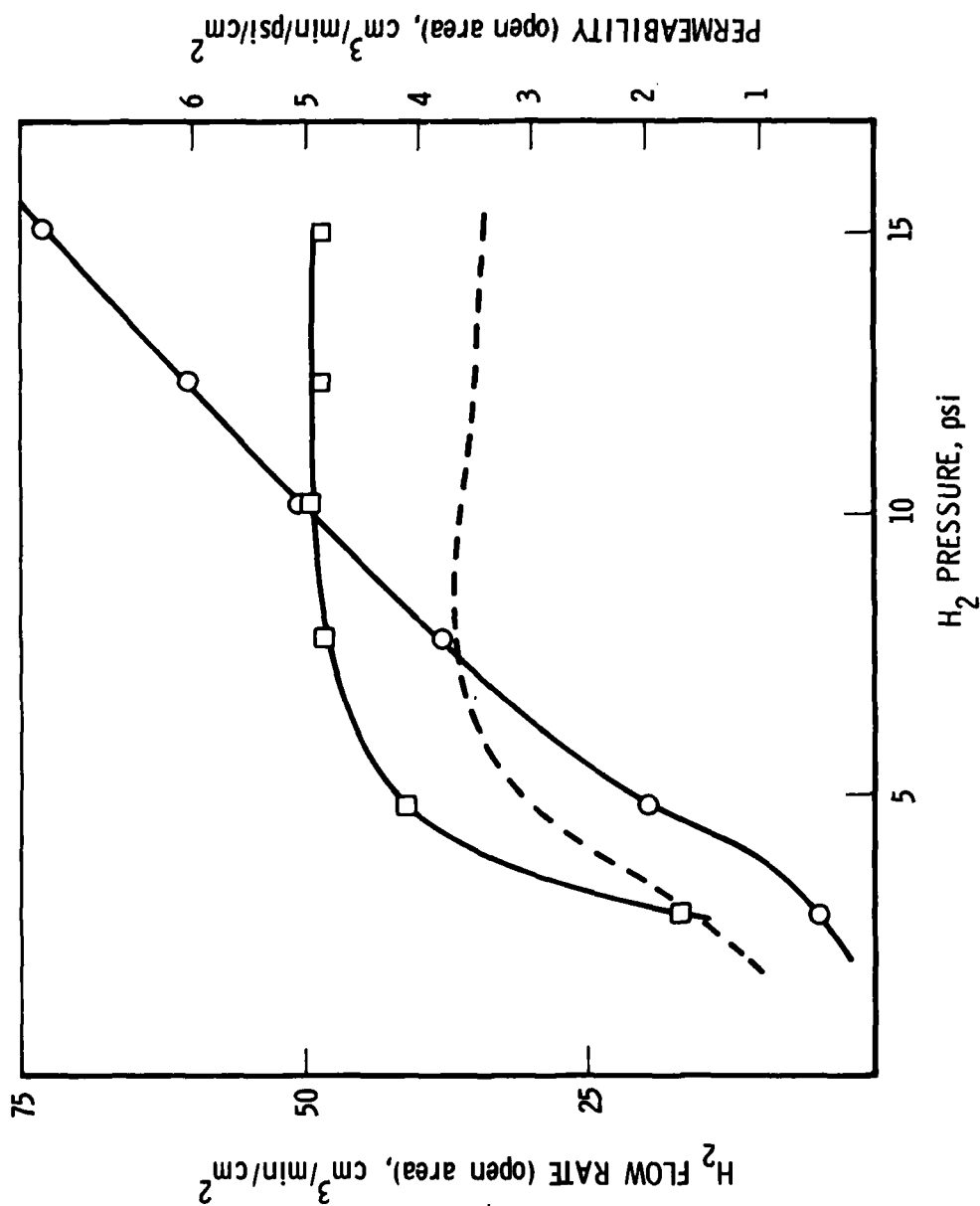


Figure 2. Permeability of 2.5 cm² of supported microporous Teflon to hydrogen at 25°C; (—○—) is H₂ flow rate, (—□—) is H₂ permeability, (---○---) is H₂/O₂ flow rate ratio plotted using the vertical scale on the right.

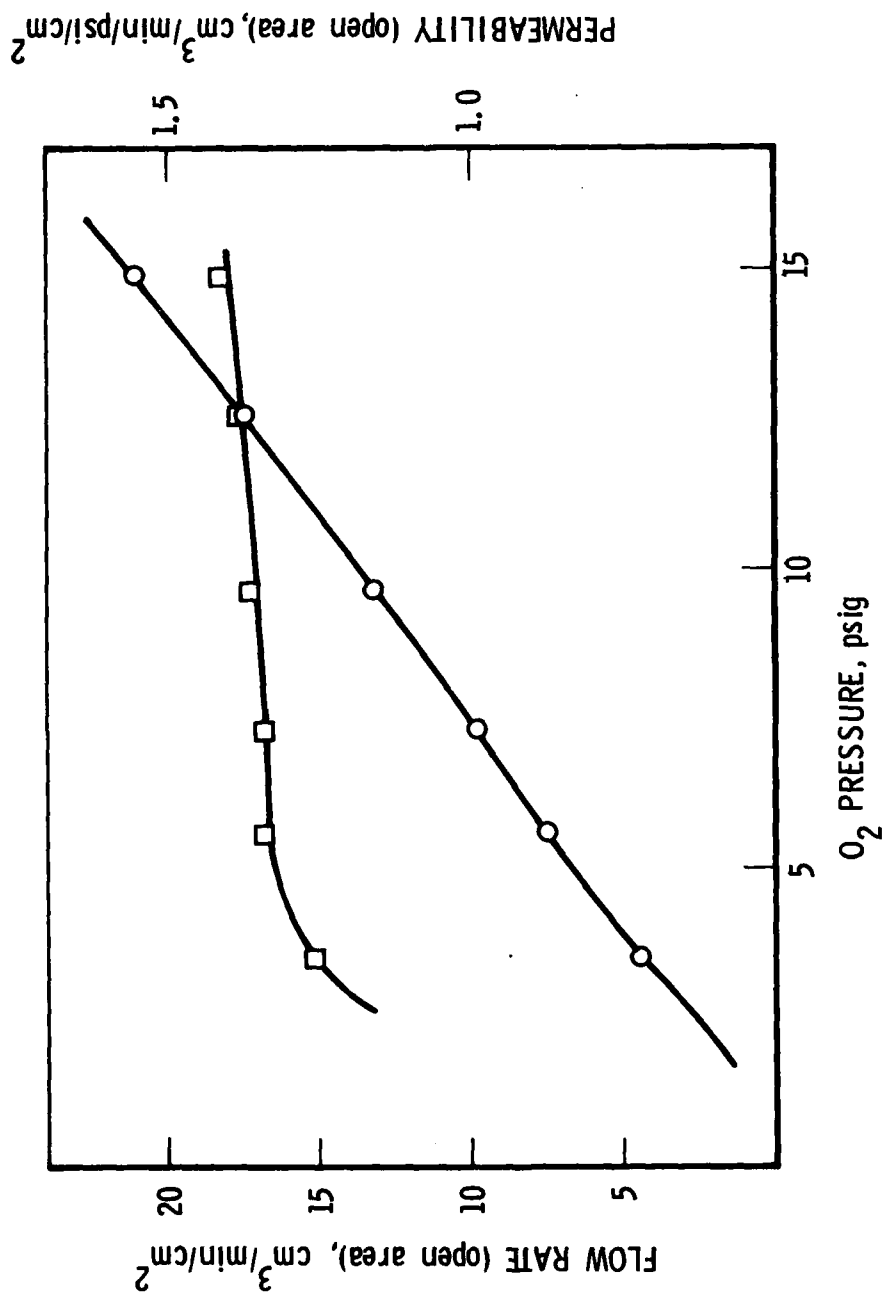


Figure 3. Permeability of 2.5 cm² of supported microporous Teflon to oxygen at 25°C; (—○—) is O₂ flow rate, (—□—) is O₂ permeability.

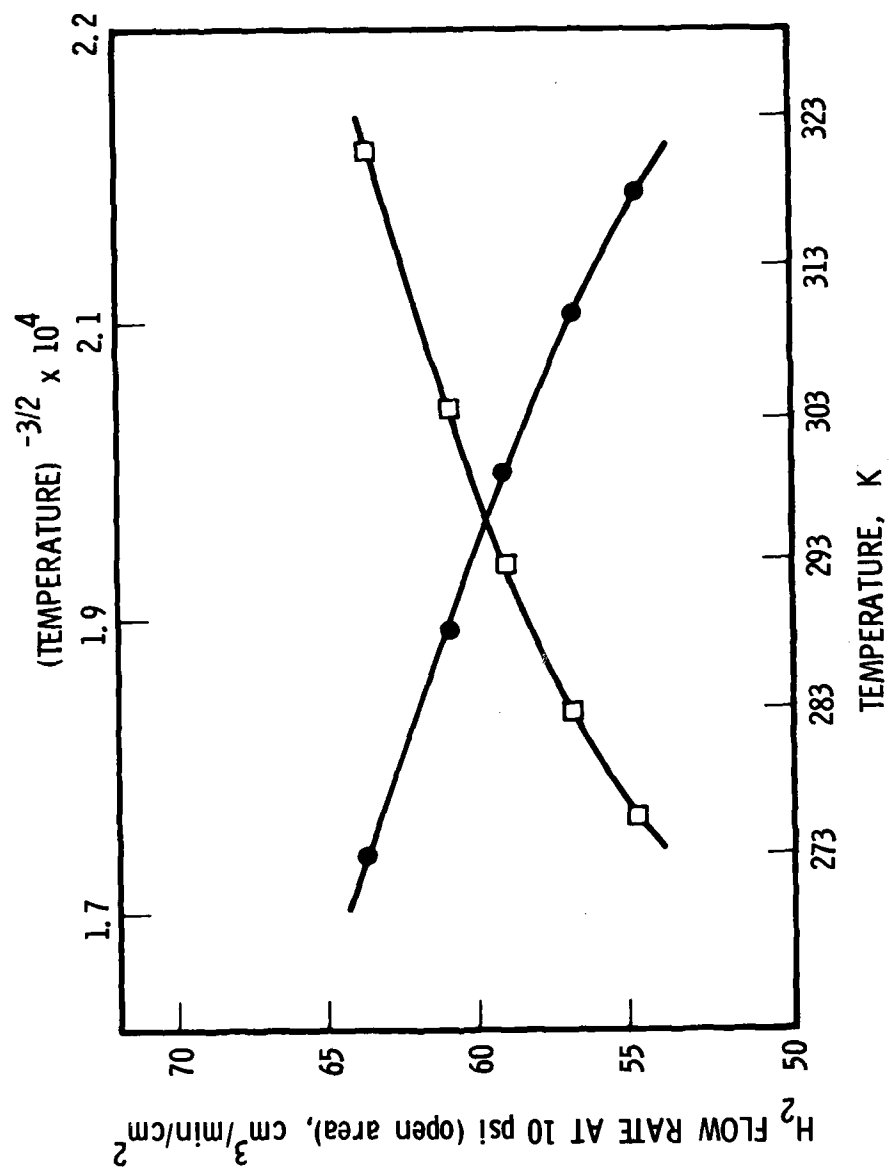


Figure 4. Temperature dependence (—●—) of H₂ flow rate through 2.5 cm² of microporous Teflon at a pressure of 10 psi. The flow rate is also plotted (—□—) against (Temperature)^{-3/2}.

function of $T^{-3/2}$ should yield a straight line, since the kinematic viscosity³ is proportional to $T^{3/2}$. This plot, presented in Figure 4, shows pronounced curvature at the higher temperatures. It may be concluded that, as the temperature is increased, the microporous Teflon material is changing such that its permeability to gas is diminished. This change is not large, however, and is likely to arise from the material softening upon heating. Softening could tend to enhance the cold flow of the Teflon such that pores may be partially blocked.

In Figure 5, scanning electron microscope photographs of the microporous Teflon surface are shown. These photographs indicate that the surface has a sintered type of structure with pore surface openings on the order of several microns in diameter. Measurements indicated that microporous Teflon to have a density of 1.48 g/cm^3 , as compared with about 2.1 g/cm^3 for Teflon. The microporous Teflon is therefore expected to be about 25 to 30 percent void volume. If a value of 29 percent void volume is used and it is assumed that the length of each pore is roughly twice the separator thickness (35 mil), the average pore size may be estimated from the permeability data for hydrogen in Figure 2. At 3 psi, viscous flow appears to adequately describe the hydrogen flow through the separator at a rate of $11 \text{ cm}^3/\text{min}$. The Poiseuille equation for viscous flow may be used to calculate the pore diameter corresponding to this flow rate:

$$d^4 = 16^2 NL \eta RT / \pi P^2 \quad (1)$$

where

d = pore diameter in cm

N = flow rate through a single pore in moles/sec

L = pore length in cm

³ D. E. Gray, ed., American Institute of Physics Handbook, McGraw-Hill Book Co. Inc., New York, 1957, Chap. 2, pp. 203-205.



Figure 5. Scanning electron microscope photographs of the microporous Teflon surface at 20 μm (left) and 10 μm (right).

η = viscosity of H_2 in poise

R = gas constant 8.314×10^7 erg/K mole

T = temperature, K

P = pressure in dyn/cm^2

If we assume cylindrical pores, the flow rate for a single pore is given by

$$N = N'/Z = N'\pi d^2/4AF \quad (2)$$

where

N' = total flow rate for all pores in a separator having surface area A and fractional void volume F

Z = total number of pores

Combining Eqs. (1) and (2) gives

$$d^2 = 64N'L\eta RT/P^2AF \quad (3)$$

Using the flow rate of H_2 at 3 psi, we compute a value of 0.47 μm for the average pore diameter in the bulk material. This estimate is in rough agreement with the surface pore sizes shown in the photographs of Figure 5, and substantiates the premise that a viscous flow regime is reasonable for hydrogen at pressures below 4 psi.

When O_2 was bubbled through KOH electrolyte, water vapor corresponding to about 80 percent saturation was freely passed through the microporous Teflon along with the gas. This loss of water from the cell amounts to about 0.015 g/hr for a gas flow rate of 27.3 cm^3/min . When electrolyte was covering the separator at a pressure of 11 psi, no electrolyte passage through the separator could be detected in a 4-hr experiment. This corresponds to an electrolyte permeability of less than 0.03 g/day.

Therefore, loss of water vapor through the microporous Teflon separator appears just as important as direct loss of electrolyte through the separator.

The gas permeability of microporous Teflon that was wetted with electrolyte was studied. The porous Teflon surface was wetted by inverting the sample holder shown in Figure 1 so that the KOH reservoir covered the separator surface. With KOH covering the entire surface, the microporous Teflon had negligible gas permeability. When the surface was drained of KOH electrolyte, the membrane regained 98 percent of its original gas permeability within 1 min and 100 percent within 5 min (10 psi applied pressure). The microporous Teflon surface therefore appears to rapidly clear itself of electrolyte after being wetted.

A more severe test is conducted under foaming conditions, where bubbles are continuously breaking on and wetting the microporous Teflon surface. Using a vigorously foaming KOH electrolyte at an applied pressure of 10 psi, we were able to decrease the permeability of the surface to hydrogen by about 60 percent. This decrease in permeability was due to the finite length of time required for the separator surface to clear itself of electrolyte after each bubble bursts on the surface. The magnitude of the permeability under foaming conditions will depend on the size and frequency of the bubbles, and therefore must be critically evaluated for the specific foaming conditions and cell design in a particular battery. It was also discovered that wetting (cleaning) the microporous Teflon with a solvent such as ethanol resulted in approximately a 5 percent greater gas permeability.

Finally the burst characteristics of microporous Teflon were investigated using a 2.5-cm² disc of separator material. With wire support (8-mesh, 0.028-in. wire diameter), this separator would not burst at 30 psi. With no wire support, the separator distended outward until it burst at about 20 psi. As the separator distended outward, the H₂ permeability increased tremendously and became too great to measure before the separator burst. Such extreme distension of the microporous Teflon membrane

appears to be largely irreversible. A more controlled method for rupturing the separator at high pressures is indicated in Figure 1. A sharp wire was soldered into the tube above the separator. As the pressure increased, the separator distended outward until it was punctured by the pointed wire. The pressure at which the separator is punctured will be determined by the separator area and by the distance between the separator surface and the pointed wire. For a separation of 1, 2, and 7 mm, the test sample burst at 4.5, 9, and 13 psi, respectively. Further testing needs to be done with a separator that is the actual size of the battery cell vent. (This vent would be smaller than 2.5 cm^2 .) This testing would determine the required distance between the separator and the pointed wire that would result in the separator being punctured at approximately 22 psi.

E. SEPARATOR EVALUATION

The gas permeability characteristics of microporous Teflon appear to be adequate for the requirements of a silver zinc battery cell vent. At the highest allowed temperatures, the H_2 permeability is four times greater than required, and the O_2 permeability about ten times greater than required. These permeabilities will allow a liquid-gas separator with a 0.5 cm^2 area to meet the stated gas permeability requirements with no support. (The test sample was 2.5 cm^2 with a wire mesh support with 80 percent open area.) The gas permeability of the microporous Teflon is only impaired while electrolyte is in contact with the sample surface. The surface, however, will clear itself of electrolyte within 1 min. Specifically, during foaming conditions, where the surface is repetitively wetted by bubbles, the gas permeability is impaired. Gas permeabilities must be determined during actual battery foaming to evaluate how much the permeabilities are diminished. Microporous Teflon seems to have very little permeability to electrolyte at an applied pressure of 11 psi. This is an ideal characteristic for a liquid-gas separator, the result being that loss of fluid from the electrolyte is likely to be controlled by the loss of water

vapor through the separator. Test results that the separator can be punctured at the desired pressure of 22 psi. However, tests must be carried out with the actual vent assembly to establish the appropriate parameters enabling the separator to be punctured at the correct pressure.

The pore size in the microporous Teflon is an important parameter. If the pores are too large, electrolyte will be passed; if they are too small, insufficient gas permeability will result. The pore size required to pass electrolyte at the maximum pressure of 15 psi may be calculated from the surface tension of electrolyte⁴ ($\gamma \approx 90$ dyn/cm), assuming the Teflon surface is not wetted:

$$r = 2\gamma/P = 1.74 \mu\text{m} \quad (4)$$

This calculation suggests that the pore sizes in the microporous Teflon are just small enough to prevent electrolyte flow through the separator. For optimum liquid-gas separator performance, pore sizes should range from 0.5 to 1.0 μm . This approximate range of pore sizes will ensure adequate gas permeability without allowing the electrolyte to escape through a microporous Teflon separator with a thickness of 17.5 mil.

F. RECOMMENDATIONS

Microporous Teflon appears to have nearly ideal properties for use as a liquid-gas separator in an alkaline cell vent. The specifications for this material, however, must include a hydrogen permeability of at least $60 \text{ cm}^3/\text{min}/\text{cm}^2$ of area at 25°C , an average pore size no larger than 1 μm , and a thickness of 17.5 ± 1 mil. Additional testing of the material in the cell vent assembly is needed to determine the distance required above the separator for the needle that punctures the separator at high pressures, and also to evaluate the effects of foaming on the gas permeability. A clean

⁴D. E. Gray, ed., American Institute of Physics Handbook, McGraw-Hill Book Co. Inc., New York (1957), Chap. 2, p. 177.

piece of this material that has an area of at least 0.5 cm^2 is recommended for separator use in the silver zinc battery cells. Because of the small size of this liquid-gas separator, no support should be required.

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