Measurement of Gas Permeability of Polymers. I. Permeabilities in Constant Volume/Variable Pressure Apparatus

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Synopsis

A constant volume/variable pressure gas permeability apparatus is described that provides accurate determination of permeabilities ranging from less than 10^{-1} to 10^{6} centibarrers. Metal construction, variable temperature control, adjustable downstream pressure and constant volume, and a differential pressure transducer with automatic recording are design features that permit detailed permeability studies under a variety of environmental conditions. Pressure effects on polymer films have been investigated up to 1000 psi, and the relation of gas concentration to permeability has been studied by varying the downstream pressure and volume conditions. The high feed pressures have significantly shortened the time required to obtain meaningful data on low-permeability materials after steady-state conditions are achieved, and the variable-temperature control has permitted evaluation of temperature-related phenomena.

INTRODUCTION

Ample treatments of permeability theory may be found in many texts and articles.[1-7] Of particular value are the work of Rogers[8] with its extensive bibliography and the treatment of Stern,[9] which includes sections on practical gas separators. The three basic methods for determining gas permeability of membranes are the constant pressure/variable volume procedure (e.g., Linde cell), the constant volume/variable pressure or manometric procedure (e.g., Dow cell), and the carrier gas procedure in which the permeate diffuses into a carrier gas which is subsequently analyzed. The last two methods are highly adaptable, and the number of variations in measurement methods multiply as experimenters devise new procedures to fit their particular objectives. A number of devices for each basic type are purchasable (variable volume cell, Custom Scientific Inst., Inc. and American Instrument Co.; variable pressure cell, Custom Scientific Inst., Inc.; concentration-carrier gas cell, Envirotech Corp.). Descriptions of others may be found in references.[2-9]

Although the instruments described previously are good, most appeared to lack one or more features desired for the wide range of studies contemplated. It was thus the object of this work to develop a constant volume/variable pressure system containing components and provisions that would permit (1) operation to 1000 psi feed pressure, (2) temperature control from ambient to

$100°C$, (3) accurate measurements from less than 10^{-1} to 10^6 centibarrers, (4) variation of initial permeate-side pressure from vacuum to high pressure, (5) use of mixed gas feed with provision for sampling for external analysis, (6) internal stirring of mixed gas feeds to prevent possible concentration polarization, and (7) automatic recording.

DETAILS OF APPARATUS

The components of a permeation testing station include the test cell, vacuum system for film conditioning, gas feed system, downstream constant-volume cavity, pressure transducer, recording system, and environmental control parts. With the exception of a portion of the vacuum system which is not subject to pressure, all components including valves and tubing are of 304 stainless steel except three brass O-ring connectors. The test cell lines and valves are operational to 1000 psi with appropriately higher burst strength ratings.

Permeation System

A schematic diagram of an individual unit is shown in Figure 1. The film is held between the cell feed cavity (B) and support flange (A). Gas permeating the film passes out of the cell through a channel connecting to a cubical "distribution" block (C) with holes drilled through each face to a common center. The volume from the film through the distribution block to the valves V_1–V_4 comprises the fixed-volume downstream cavity in which the pressure build-up of the permeating gas is measured. This volume is approximately 12 cc. The bottom hole from the block connects through a toggle valve (for quick opening) to a larger volume (capacity ca. 150 cc) (E) for use with high-flux films.
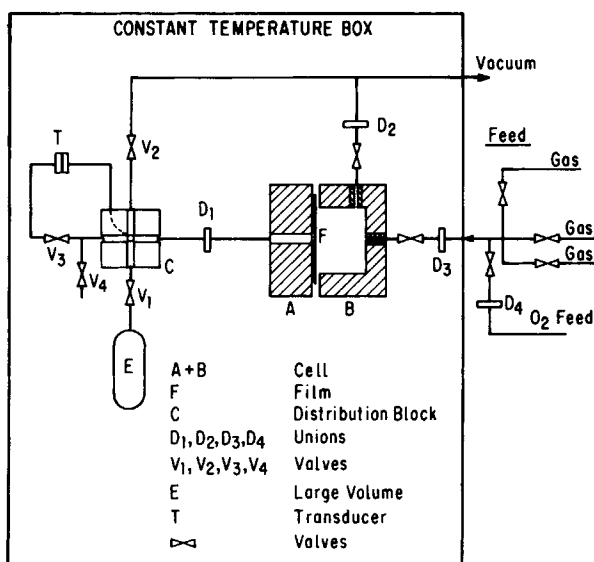

Fig. 1. Pressure permeation apparatus. Schematic Diagram.

The pressure transducer (differential type) is attached to the rear hole in the block, and the reference side of the pressure transducer is connected to the left exit hole through valve V_3. When this valve is open, the entire cavity can be evacuated through valve V_2 and connecting tubing leading from the top hole to the vacuum system. This tubing joins with a similar line from the feed cavity portion of the cell so that both sides of the cell can be connected—either for evacuation or to equalize pressure. V_4 is the exit port to a gas sampler for external chemical analysis. The cell containing the film can be easily removed by opening the O-ring connectors (D_1 and D_2) and a union (D_3) on the feed line.

The important valves are V_1, V_2, and V_3. The toggle valve V_1 permits quick change of volumes to adjust to permeating conditions during test. V_2 must be a leak-tight valve to seal the cavity from the vacuum line. Either a toggle valve or a bellows valve has been satisfactory. V_3 must be a leak-tight, quick-opening valve that can be opened quickly to protect the transducer from overpressuring if a film should fail. It also permits zeroing the pressure transducer at any desired pressure level in the permeate cavity—a feature useful in long-term permeability studies or in evaluating gas concentration effects. A Magnalatch, a remotely operated magnetic valve manufactured by Skinner Co., has been ideal since, unlike a solenoid valve, no current flows through the coils when the valve is operating and hence there is no heat input to the metal. Heat would cause pressure change in the closed cell, thereby altering the apparent pressure and permeability.
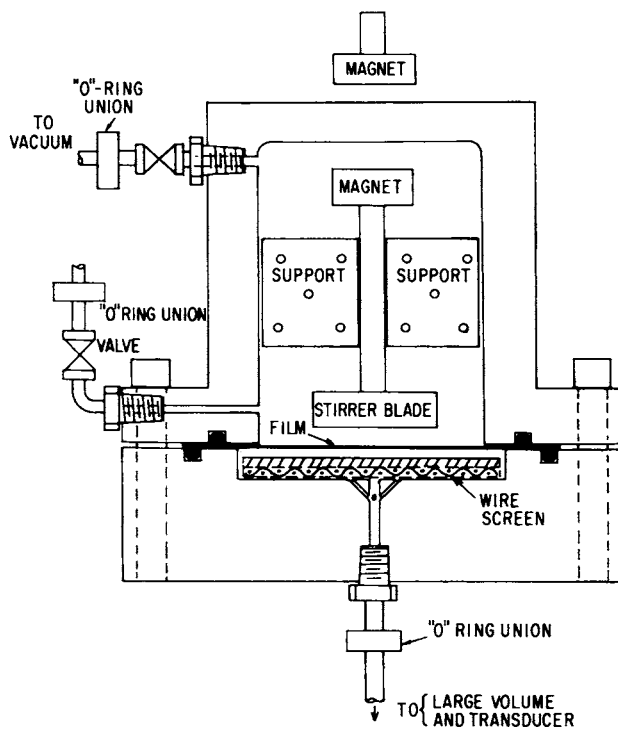

Fig. 2. Gas permeation cell (magnetic stirring unit optional).

Permeation Test Cell

The cell design is shown in Figure 2. The test film is clamped between a supporting metal flange and the cell body containing the feed cavity and is sealed with O-rings. The feed cavity accommodates an externally driven magnetic stirrer for use with mixed gases to minimize possible concentration polarization phenomena in high-flux systems. To permit unrestricted gas collection on the down-stream side of the film, a Regimesh (Pall Trinity Corporation) Type NK screen consisting of a nominal 2-micron mesh laminated to a coarse supporting screen is inserted between the film and the support flange. The screen has sufficient strength to bridge the small diameter holes in the flange that connect with the central channel to the transducer.

Vacuum System

The vacuum system is conventional, utilizing a mercury diffusion pump, a high-capacity forepump, and liquid nitrogen-cooled traps. Although evacuation below 10^{-3} mm is not essential, lower values decrease conditioning time. If atmospheric testing is undertaken, evacuation may be omitted. Since the permeate cavity is isolated during test, cold-finger effects and other vacuum system contamination problems are eliminated.

Feed System

To obtain sufficiently accurate control of feed gas pressure, the test gas is directed through an appropriate pressure-reducing valve and monitored on one of three (low, medium, and high) pressure gauges with suitable protective pressure limiters. A gas manifold and purging system simplify frequent changes from one feed to another. For safety purposes, oxygen is introduced from an entirely separate system. Suitably located check valves, rupture disks, pop-valves, and flash arrestors provide for safe operation.

Pressure-Sensing System

Accurate pressure sensing is the key to good measurements. Use of a pressure transducer in place of a Dow cell-type manometer permits safe operation (in case of film failure) up to high pressure at constant volume since the transducer volume does not change significantly with pressure. A differential transducer also permits operation starting at any desired pressure level. All that is required is that the reference and test sides start within the transducer range. A highly versatile, compact transducer is the Whittaker Corporation variable reluctance Model P7D operated by a carrier-demodulator Model CD. The advantage of this type of sensor is that the metal diaphragm has no attached wires (as in the resistance type) but lies between two coils which sense any deflection of the diaphragm. Choice of diaphragm thickness governs the sensitivity range. If damaged, the diaphragms can be readily and inexpensively changed in the laboratory. Resistance transducers must be returned to the factory. Diaphragms with useful range to about 250 mm are rugged yet have the sensitivity required for use with low fluxes.

The signal from the carrier-demodulator is recorded on a Hewlett-Packard recorder Model 7100B. It offers a range of chart speeds and sensitivity convenient for handling a wide range of film permeabilities. With the carrier-demodulator set at 10 volt d.c. output and the recorder at 1 volt, a transducer with a nominal 5 psi diaphragm (0–250 mm Hg range) will have a sensitivity of about 0.1 mm Hg/0.1 in chart deflection (about 10 mm full scale). The demodulator signal may alternatively be directed to a computer terminal for automatic measurement.

Environmental Control

Since gas permeability is sensitive to temperature change, the cell was placed in a constant-temperature box. The range employed in this work was from ambient to 100°C. Temperatures are regulated with Athena proportional controllers since it was found that on–off heat cycles from a bimetallic sensor and an Aminco relay would cause sufficient temperature variation in the constant volume of the cell to give a fluctuating signal on the recorder. Most measurements described in the experimental section were at 30°C.

OPERATIONAL PROCEDURES

Two calibrations are essential. The first is the response of the transducer to pressure and the second, the measurement of the constant volume. The transducer response may be determined by routine methods using an external mercury manometer or McCleod gauge as a primary standard. Accurate measurement of the down-stream volume is readily accomplished by attaching a small (10 cc) calibrated flask near the cavity and by using standard gas law expansion methods in conjunction with the transducer and recorder.

Operation of the test cell for standard time-lag or diffusivity measurements follows the procedures normally required for such tests, and detailed discussion of the valving steps peculiar to this particular arrangement are unnecessary. The elements of film conditioning theory and time required to reach steady-state conditions have been amply described,[4,10] but conditioning may be omitted if fluxes are high or if the equipment is operated at atmospheric or higher down-stream pressure.

In standard operation, films are usually conditioned until vacuum readings of less than 5×10^{-4} mm are obtained and a low "baseline" drift—a test of the closed permeation cell with no applied feed gas—is obtained. A small but constant drift may be encountered if trace volatiles are still diffusing from the film specimen or trace leakages passed the O-ring seals exist. With a properly installed and conditioned film, the drift rate is usually less than 5% of steady-state permeation and is well below 1% for permeabilities above 50–100 cB. However, since it is normally constant, the actual drift is routinely determined and correction is applied to the calculation.

Following baseline determination, feed gas is introduced and the permeation test begun with the reference side of the transducer closed. Appropriate choice of recorder chart speed and sensitivity in combination with selection of the desired downstream volume size permit establishment of a convenient pressure/time line slope. When diffusion constants are not being de-

termined, permeabilities at successively different pressures can all be obtained in a continuing operation simply by rezeroing the recorder and making any desired recorder sensitivity changes. Similarly, measurements at higher than vacuum down-stream pressure can easily be made by opening and reclosing the reference side of the transducer to equalize pressure and reattain a full transducer pressure range, which in the case of a 5-psi diaphragm is 200–250 mm. If independent analyses of mixed gas permeation are desired, gas samples may be taken in sampling loops through the auxiliary sampling port.

The dimensions of the test cell required a film specimen 7.9 cm in diameter, and the calculated effective film area was 19.7 cm^2. By use of the appropriate gas laws, cell constants, and sensitivity factors related to the transducers and recording systems, the following permeability equations were derived for calculation of $P_{(\text{gas transmission rate})}$ and $P_{(\text{centibarrers})}$ at 30°C. Gas transmission rate (GTR) and Barrer permeability units are as defined in ASTM standards[7]:

$$P_{GTR} = \left[\frac{(P_2 - P_1)(V_2)}{t_2} - \frac{(D_2 - D_1)(V_1)}{t_1} \right] \frac{C_x}{p} \qquad (1)$$

and

$$P_{cB} = (P_{GTR})\,(0.6)\,(\text{film thickness, mils}) \qquad (2)$$

where $P_2 - P_1$ = steady-state pressure-related recorder displacement in time t_2 at recorder sensitivity V_2; $D_2 - D_1$ = baseline pressure-related recorder displacement in time t_1 at recorder sensitivity V_1; C_x = cell constant incorporating all conversion and calibration factors; p = the pressure differential across the membrane in psia; and 1 centibarrer (cB) = $[10^{-12}\text{cm}^3$ (S.T.P.)· cm/cm^2·sec·cm Hg].

EXPERIMENTAL EXAMPLES

Accuracy of Determinations

Accuracy of permeability determinations depends on equipment calibrations, sensitivity and control, as well as level of permeability and quality of film specimen. Very low permeabilities are subject to high uncertainties because small extraneous errors are disproportionately large. Table I contains data illustrating the reproducibility of permeabilities of two polyethylene samples placed in two cells and using both small and large volumes. The maximum spread was 5%. In another series of 17 successive measurements over a period of three days on a pressed film of poly(ethylene terephthalate) at 1000 psia O_2, the average value was 6.3 ± 0.3 cB, with the exception of two measurements at 7.0. The deviation from the average was 4.7%. In a similar series on a sample of Lopac [poly(methacrylonitrile/styrene)], the average O_2 permeability was 0.47 ± 0.02 cB in six determinations over four days. Data below 0.1 cB are subject to larger errors.

Comparison of data from different laboratories is difficult because film preparations, history, and morphology are always different and variations in test methods and inherent, apparatus-induced errors occur. See, for exam-

TABLE I
Reproducibility of Permeability Data[a]—Polyethylene

Test cell	Film A	Film B	Diff, %
1S[b]	299	302	1.0
1L[c]	304	298	1.9
2S	292	296	1.5
2L	305	297	2.7

[a] Methane, 115 psia, 30°C. Data in centibarrers (cB).
[b] Small volume.
[c] Large volume.

ple, a recent analysis of Dow cell measurement methods.[11] Table II contains a comparison of several results obtained in this work with published literature data. Since a statistical analysis of variables test showed no significant differences, it may be concluded that the agreement is good for unrelated film specimens.

Permeability Range

Although a high percentage of permeabilities of typical polymer structures lies between 1 and 1000 cB, permeabilities of barrier films and porous materials are outside this range. The data in Table III illustrate the capability of the apparatus to obtain these data. In all cases, a 5-psi (~250 mm) transducer diaphragm was used.

High feed pressure and the capability of restarting a test at any time by rezeroing the transducer are assets in the study of low permeabilities. Although little can be done to decrease the time required to reach steady state other than reduce film thickness, high pressure decreases final measurement times. This is not only a great convenience but decreases errors due to adventitious pressure development which is also time related and will be small

TABLE II
Comparison of Data with Literature Permeabilities[a]

Material	Permeability, cB			
	H_2	CH_4	O_2	N_2
Mylar 100[d]	60[b]	—	2.0[b]; 3.0[b]; 4.5[c]	—
Mylar 100S	(67)	—	(2.9)	—
Polyethylene	1200[c]	290[b]; 370[b]	290[b]; 395[c]	100[b]; 136[b]
Polyethylene	(1000)	(325)	(420)	(140)
Capran 77C[e]	94[b]	—	—	—
Capran 77C	(88)	—	—	—
Polypropylene	—	—	230[b]	44[b]
Polypropylene	—	—	(200)	(49)
Polystyrene	—	—	240[b]; 250[b]; 180[b]	—
Polystyrene	—	—	(250)	—

[a] Data from this work in parentheses; temp. 30°C.
[b] H. J. Bixler and O. J. Sweeting, ref 4.
[c] H. Yasuda, ref. 5.
[d] Commercial poly(ethylene terphthalate) film.
[e] Commercial nylon 6 film.

TABLE III
Permeabilities of Selected Materials

Material	Gas	Pressure, psia	Permeability[a]
Vinylon[b]	He	1015	.71
Vinylon	H_2	1015	.065
Vinylon	CH_4	1015	.003
Vinylon	O_2	1015	.003
Poly(AN/MA)[c]	He	1015	38.0
Poly(AN/MA)	H_2	1015	9.1
Poly(AN/MA)	O_2	1015	.036
Poly(AN/MA)	N_2	1015	.004
Polyethylene	H_2	115	1000.0
Polyethylene	CH_4	115	325.0
Polyimide[d]	H_2	40	1.0×10^4 [e]
White Paper	CH_4	35	6.0×10^7

[a] In centibarrers at 30°C except as noted.
[b] A commercial poly(vinyl alcohol).
[c] Poly(acrylonitrile/methyl acrylate), ca. 97.5/2.5.
[d] Asymmetric film from pyromellitic dianhydride and 4,4'-diaminodiphenyl ether prepared as described in C. W. Alegranti, D. G. Pye, H. H. Hoehn, and M. Panar, *J. Appl. Polym. Sci.*, **19**, 1475 (1975).
[e] In GTR units because of asymmetry.
[f] A highly filled glossy paper.

for short times. When very low permeabilities are involved (e.g., < 0.01 cB as in Table III), the most accurate procedure is to reevacuate the downstream volume after steady state is achieved and then begin the actual permeation test. After an appropriate interval, reevacuation of the cavity will cause the recorder pen to return to zero, and this drop will be a precise measure of the pressure developed in the period. This is a maximum value, and a small correction can be applied for adventitious pressure by repeating the procedure with vacuum on the feed side of the membrane. For long-term low permeability tests in which the lag time may be 4 hr or more, this procedure avoids inclusion of time-lag period in the permeation calculation. In situations of this type, the line curvature is so low that achievement of steady state cannot be visually determined. If extensive barrier film study is to be undertaken, the downstream small volume may be decreased to 4–5 cc.

If permeabilities above 10^5–10^6 cB are consistently encountered, the large volume may be increased and low feed pressure used. Revision of the film support and gas exit system may be advisable to ensure rapid pressure equilibration. Data on a white pigmented paper are shown in Table III to illustrate the measurement of very high permeabilities.

Permeability as a Function of Downstream Pressure

By appropriate valve manipulation the nature of the downstream gas may be controlled before initiation of a test and the absolute pressure determined either from the vacuum or pressure systems. The downstream pressure may thus be subtracted from that of the feed pressure to determine the actual Δp for the permeation. The data in Table IV are examples of experiments aimed at determining the effect of downstream gas concentration on perme-

TABLE IV
Effect of Downstream Pressure on Permeability[a]

Gas	Feed pressure, psia	Down-stream pressure, psia	Per-meability, cB
O_2	1015	0	6.1
O_2	1015	14.7	6.5
CO_2	615	0	53.0
CO_2	615	14.7	53.0

[a] Data on poly(ethylene terphthalate).

ation. In these tests, the permeability of poly(ethylene terephthalate) during short exposure times to O_2 and CO_2 was not altered by a significant concentration of gas. Experiments of this type are important for concluding when successive permeation experiments may be undertaken without reevacuation of the downstream cavity and for determining permeabilities when there is significant gas/film interaction.

Permeability as a Function of Pressure

The effect of pressure on permeability of permanent gases is dependent on the gas, the film structure, and the pressure involved. Stannett et al.[12] show no pressure effect of CO_2 in nylon 6, but the pressure range was less than 1 atmosphere. Stern et al.[13,14] found a positive effect (rising permeability constant with increasing pressure) for CO_2 and some other gases for polyethylene at temperatures below their critical temperature in the pressure range up to 60 atmospheres. He found no effect for helium at temperatures above the critical. We have found essentially no pressure effect for H_2 or CH_4 for polyethylene at 30°C in agreement with Stern. Data are shown in Table V. In our experience, a positive pressure effect (increasing permeability) with non-interactive gases has always been ascribable to film imperfections which give rise to pinhole effects.

Instances of negative pressure effect have been observed. The data of Table VI show a decrease of 30% when methane feed pressure was raised from 115 to 1015 psia, and in some cases the decrease has amounted to as much as 50%. Such behavior appears related to the material under test. The permeability decrease does not seem to be an artifact of the test cell in which increasing pressure forces the film so tightly against the metal support screen

TABLE V
Effect of Pressure on Permeability of Polyethylene[a]

Pressure, psia	Permeability, cB	
	H_2	CH_4
40	1000	326
115	1000	324
315	970	333

[a] At 30°C, film specimen different from that of Table I.

TABLE VI
Effect of Pressure on Methane Permeability of a Polyimide[a]

Pressure, psia	Permeability, cB[b]	
	No paper	Paper[c]
115	41.3	43.2
315	32.4	36.9
615	30.4	30.4
1015	29.3	28.5

[a] Prepared from 4,4'-oxydianiline and 3,4,3',4'-diphenylhexafluoroisopropylidine tetracarboxylic acid dianhydride.
[b] At 30°C.
[c] No. 54 filter paper interposed between film and support screen.

that the effective permeation area is decreased by the area of the screen wires since data such as those of Table VI show essentially no change when a filter paper support is interposed between the film and screen. Hydrogen permeability for this film was unaffected by pressure. A similar permeability decrease was noted for O_2 permeability through Mylar 100S in which permeability dropped from 3.5 to 2.6 cB as the feed pressure was increased from 115 to 1015 psia. Stern et al.[14] reported a small negative pressure effect for helium on polyethylene. In our experience, permeabilities of the small molecules have been relatively insensitive to pressure.

DISCUSSION

Permeabilities obtainable with the apparatus that has been described cover the range from less than 0.01 cB to greater than 10^6 cB. The manipulative features relating to feed pressure, permeate cavity volume and pressure, and differential pressure sensor operation permit study of film permeability under a variety of environmental conditions including effects of high pressure and downstream back pressure. Permeation of a gas against a downstream environment of a different type of gas may also be studied provided back diffusion through the membrane is not significant. The provision for a sampling device permits external analysis when desired.

High feed pressure is a useful feature for reducing permeation test times. Although this capability is not of great moment for high permeabilities, it is an asset for study of barrier films (cB < 0.1) since increasing the pressure from 50 psi (a value frequently used) to 1000 psi reduces the permeation time after steady state is achieved by a factor of 20 or from several days to 4–8 hr. Such time-related errors as trace gas leakage are also reduced. The method of testing barrier films described above is easily accomplished with this apparatus and possible error due to inclusion of "nonsteady state" permeation is minimized.

In addition to the measurement capabilities that have been described, precise temperature control improves accuracy and facilitates study of temperature related phenomena. For many membranes, the rate of permeability change is 3–5%/°C. Although the system used in this work was designed for operation from ambient to 100°C, simple alterations to insulation and heating and provision for cooling would easily extend the range. Data illustrating temperature effects have not been included, but experiments have shown

both the usual permeation changes as well as return to initial permeation values with return to initial conditions provided a stable membrane was studied.

Determination of diffusion constants by the standard time-lag methods are applicable to results from this equipment. The number of controllable variables such as high feed pressure, temperature and downstream cavity "back pressure" afford an excellent system for evaluating permeability behavior, particularly of condensable materials or those capable of reaction with the membrane.

CONCLUSIONS

The permeability apparatus that has been described is a sensitive and versatile instrument in which known principles and systems have been combined to provide equipment capable of measuring most of the permeation and diffusion characteristics of membranes and their response to a wide range of operating conditions. The use of pressure transducers and constant-volume cavity eliminates problems and errors associated with accurate determination of a variable volume and enhances safe operability at high pressures. The provision for automatic recording as well as sampling for independent chemical analysis add additional versatility. Accurate measurements of low permeabilities in reasonable operating times and determination of permeability changes as a function of pressure have been shown to be important results of high pressure permeability studies.

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