Air Ingress in Packages Sealed with Crowns Lined with Polyvinyl Chloride[1]

T. J. Wisk and K. J. Siebert, *The Stroh Brewery Co., Detroit, MI*

ABSTRACT

Gas chromatographic measurements of package headspace gases indicate that significant amounts of oxygen and nitrogen from air pass into bottles sealed with polyvinyl chloride (PVC)-lined crowns. This transfer occurs because of the difference in partial pressure of these gases inside and outside the package. The rate at which ingress occurs depends on the temperature, the type of gas, and the nature and dimensions of the barrier. For beer stored in air at room temperature in bottles sealed with PVC liners, the rate of ingress for oxygen or nitrogen is about 0.002 ml/day. This is larger than expected based on the permeability of PVC. The phenomenon is not observed in bottles sealed with aluminum spot crowns or in cans. Flavor evaluation suggests that flavor stability is reduced by oxygen ingress.

Key words: Bottles, Diffusion, Liners, Nitrogen, Oxygen, Permeability

The phenomenon of gas permeation through a plastic membrane is not new. It has been studied extensively in the plastic packaging industry and in academia, e.g., by Amini and Morrow at Rutgers (2). Permeation through polymers is of sufficient importance to have led the American Society for Testing and Materials to establish an official method for its measurement (1). The permeation of air through crowns was studied by Cooper in 1951 (3), but his work dealt with cork and cork-lined crowns. When plastic liners came into use, their possible permeability received little attention by the brewing industry. Our interest in oxygen and nitrogen permeation through crown liners occurred when we noted what appeared to be an anomalous increase in headspace nitrogen content with time.

[1]Presented at the 52nd Annual Meeting, Tucson, AZ, May 1986.

This manuscript was prepared for electronic processing.

EXPERIMENTAL

Samples

Commercially packaged beer in 12-oz bottles and cans or pilot plant packaged beer or carbonated water in 12-oz bottles was used for testing. Water was treated with detergent (Lab Kol, Stewart Chemical Co., Minneapolis, MN) at the rate of 0.14 g/L prior to packaging. Closures on nonreturnable and returnable bottles were of the twist-off and pry-off types respectively. Commercial crowns from several suppliers and one prototype crown were used. The crown liners tested included aluminum spot on cork, foamed polyvinyl chloride (PVC), solid PVC, and a prototype liner material.

Storage Conditions

Packaged water was stored as follows: control (no storage); four weeks at 22° C in air; two and four weeks at 38° C in air; three and six days (0.4 and 0.8 weeks) at 60° C in air; four weeks at 38° C in oxygen (30 psig); and four weeks at 38° C in nitrogen (30 psig).

Packaged beer was stored in air, in carbon dioxide at 30 psig, in oxygen at 30 psig, or in nitrogen at 30 psig. The storage temperatures employed were 0, 22, and 38° C, and storage times extended up to 24 weeks. The above atmospheric pressures were achieved by placing packages upright in 5-gal stainless steel Firestone tanks and then purging and filling the tanks with the required gas at the test pressure.

Analysis for Air Content

Headspace oxygen and nitrogen contents in the packages were determined via gas chromatography (GC) as described previously (6). Typically, six packages were analyzed at each storage condition, and the results were averaged to provide an estimate of the oxygen or nitrogen content at that condition.

Measurements of package air content were done with the Zahm shake-out procedure (7).

Flavor Evaluation

Two-way preference taste tests were used to compare the effects of storage of 12-oz bottles of beer at room temperature in air and in nitrogen (30 psig) atmospheres. A panel of 17 experienced beer tasters was used for the evaluation. Sample presentations were randomized.

Statistical Analyses

Analysis of variance was conducted with BMDP7D, a computer program for descriptive analysis from BMDP Statistical Software, Inc., Los Angeles, CA. Zahm air results were evaluated with the Wilcoxon signed rank test (5). Taste test results were evaluated with the sign test (5).

RESULTS AND DISCUSSION

Air Ingress

The results of an initial test in which commercially packaged nonreturnable bottles of beer were stored for up to 20 weeks at 0, 22, and 38° C are shown in Figures 1 and 2. According to Figure 1, the headspace oxygen content (corrected for argon as described in our earlier work [6]) decreased, although somewhat erratically, during the test period. It was interesting to note, however, that the headspace nitrogen content (Fig. 2) increased steadily at all three storage temperatures although at different rates. Packages stored at the highest temperature showed the largest amount of headspace nitrogen after 20 weeks of storage. The amount of headspace nitrogen in the package appeared to be a function of both time and temperature. Because it didn't seem likely that the nitrogenous components of beer could break down to form nitrogen, air ingress was the most likely explanation for the nitrogen increase.

Returnable bottles (12-oz long-neck) were filled with deaerated, carbonated, detergent-treated water. Water was used to avoid the consumption of oxygen that occurs in beer, and the detergent was used to help induce foaming during filling. The bottles of packaged water were stored for various times at different temperatures and then analyzed for their headspace gas content. The top portion of Table I contains the results of the headspace analyses after the various treatments. At each storage temperature, there was a progressive increase in package headspace oxygen and nitrogen content with time. A comparison of the data at 22 and 38° C at four weeks of storage indicates that the ingress rate increased with temperature.

The last two lines of data in Table I clearly demonstrate that different gases have different permeabilities through plastic. For the bottles stored in the nitrogen atmosphere, there was an increase in headspace nitrogen content of 0.29 ml in four weeks. For those bottles stored in oxygen at the same pressure, there was an increase in headspace oxygen of 0.78 ml in the same time, or almost a 3:1 difference in rate. This implies that in a bottle stored in air, where the nitrogen-to-oxygen ratio is 4:1, the amount of oxygen that gets into the package would not be just one-quarter the amount of nitrogen but more like two-thirds to three-quarters of the amount of nitrogen because of the greater permeability of oxygen.

The data in Table I also illustrate the effect that partial pressure has on permeability. Ambient air at one atmosphere contains 80% nitrogen (or 0.80×1 atm = 0.80 atm) and, similarly, 0.20 atm oxygen. If nitrogen results for the bottles stored four weeks at 38° C are compared, it can be seen that the increase was $0.471 - 0.186 = 0.285$ ml in 30 psig nitrogen (where the absolute pressure is 3 atm) and $0.278 - 0.186 = 0.092$ ml in air; this is a ratio of 3.1 times in rate of nitrogen ingress, and compares with a ratio of partial pressures of 3.0 atm/0.8 atm = 3.8. In like manner for oxygen, the ratio of ingress rates is $(0.851 - 0.070)/(0.118 - 0.070) = 16.3$, whereas the

TABLE I
Headspace Oxygen and Nitrogen Contents (ml STP) in 12-oz Returnable Bottles Sealed with Commercial Crowns Lined with Polyvinyl Chloride and Stored in Air (Except as Specified) at Three Temperatures[a]

Storage Time (weeks)	22°C		38°C		60°C	
	O_2	N_2	O_2	N_2	O_2	N_2
0	0.070	0.186	0.070	0.186	0.070	0.186
0.4	···	···	···	···	0.077	0.224
0.8	···	···	···	···	0.084	0.258
2	···	···	0.098	0.246	···	···
4	0.096	0.231	0.118	0.278	···	···
4[b]	···	···	0.060	0.471	···	···
4[c]	···	···	0.851	0.184	···	···

[a] Bottles contained detergent-treated carbonated water.
[b] Stored in 30 psig nitrogen.
[c] Stored in 30 psig oxygen.

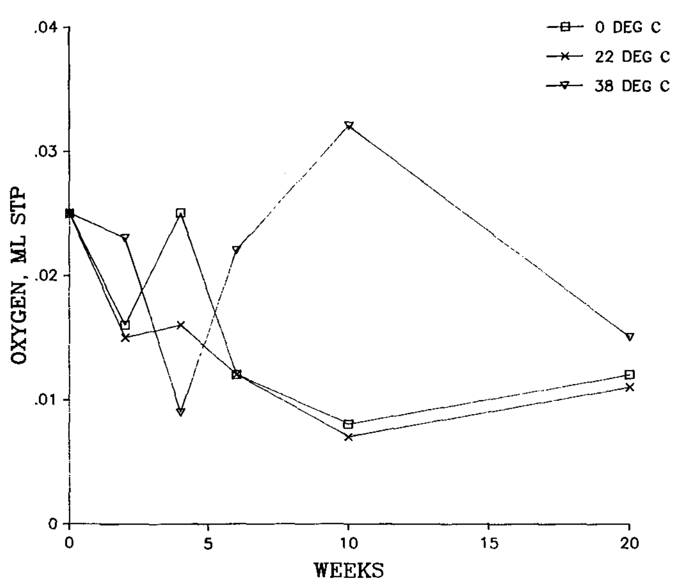

Fig. 1. Headspace oxygen content in 12-oz nonreturnable bottles of beer versus weeks of storage. The bottles were sealed with regular commercial twist-off closures lined with polyvinyl chloride and were stored in air at three different temperatures.

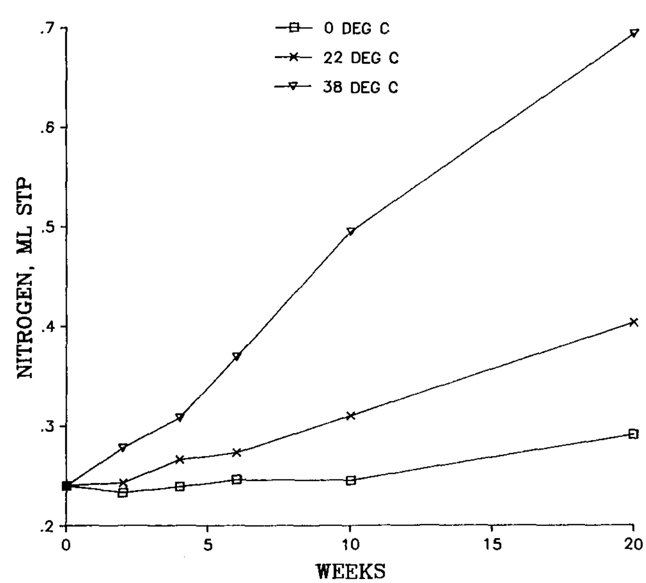

Fig. 2. Headspace nitrogen content in 12-oz nonreturnable bottles of beer versus weeks of storage. The bottles were sealed with regular commercial twist-off closures lined with polyvinyl chloride and were stored in air at three different temperatures.

ratio of partial pressures is 3.0 atm/0.2 atm = 15.0. It is clear that the transmission of the gas across the liner is related to partial pressure.

A check to see if ingress occurs in cans was done by comparing the headspace nitrogen contents of beer-filled cans and bottles stored in air, CO_2 (30 psig), or N_2 (30 psig) for up to four weeks at 38° C. While oxygen is the substance of primary concern, its increase resulting from ingress is offset by its consumption by the beer. We chose to measure nitrogen and assume that oxygen ingress occurs in parallel as seen in water. The results for bottles

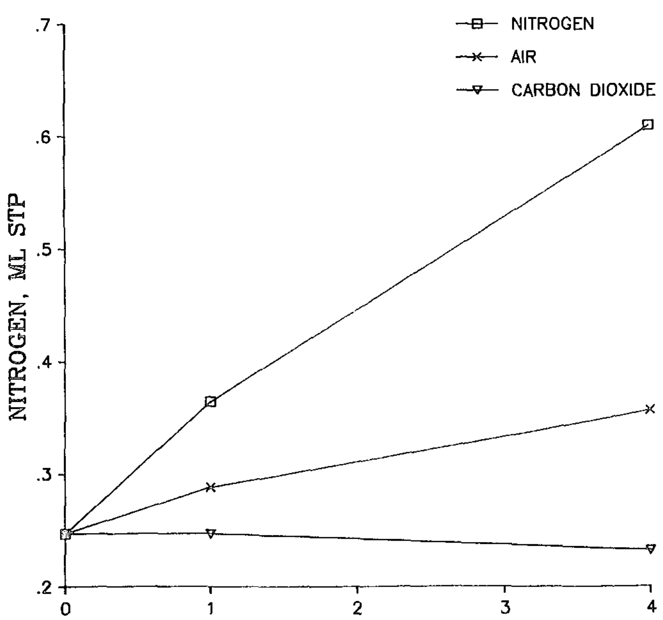

Fig. 3. Headspace nitrogen content in 12-oz nonreturnable bottles of beer versus weeks of storage. The bottles were sealed with regular commercial twist-off closures lined with polyvinyl chloride and were stored at 38° C in three different gases.

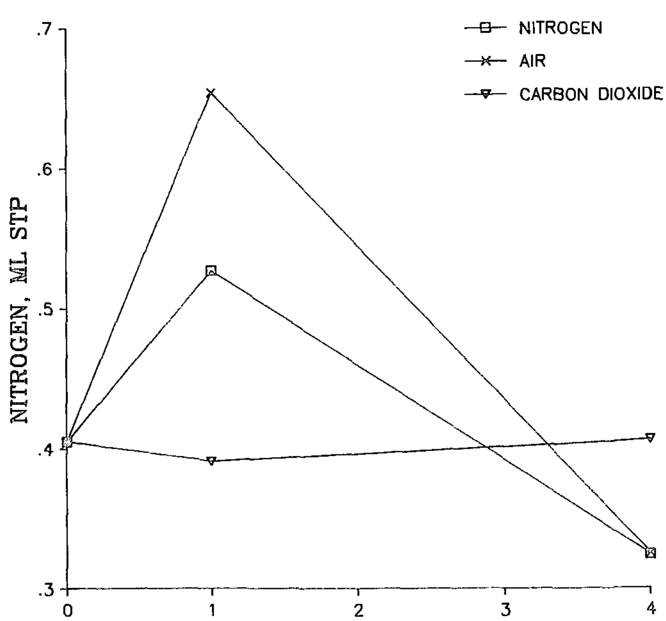

Fig. 4. Headspace nitrogen content in 12-oz cans of beer versus weeks of storage. The cans were stored at 38° C in three different gases.

(Fig. 3) were similar to those observed in the experiment with bottled water, i.e., the headspace nitrogen increased in packages stored in either air or nitrogen. The slight decrease in package headspace nitrogen content that was observed for the bottles stored in CO_2 likely occurred because in this case the partial pressure of nitrogen is higher in the package than in the surrounding atmosphere. There is thus a tendency for the nitrogen to "leave" the package headspace.

The results obtained with cans (Fig. 4) are confusing. After one week of storage at 38° C in air or 30 psig nitrogen, the headspace nitrogen concentration had increased, while at later times at the same temperature, it was lower. Our preliminary conclusion was that ingress does not occur in cans. A later test with commercially filled packages in which the total package air content was measured initially and after room temperature storage (up to 14 weeks) via the Zahm shake-out procedure (Table II) independently confirmed that gas ingress does occur. It was statistically significant at the 95% confidence level in bottles, but not in cans. Examination of the nonreturnable and returnable bottle results in Table II suggests that ingress may be more pronounced in the latter.

For some of the packages analyzed by the Zahm technique, carbon dioxide was also measured (data not shown in Table II), and it was found to decrease by about 0.11 volumes in 24 weeks. Because the partial pressure of carbon dioxide is higher inside the package than outside, there would be a tendency for the carbon dioxide to pass from the bottle to the atmosphere.

The effectiveness of aluminum as a barrier was checked by comparing headspace nitrogen contents of bottles of beer sealed with aluminum spot crowns to bottles sealed with PVC-lined crowns. Table III shows that significant nitrogen ingress did not occur in bottles sealed with aluminum spot crowns. The barrier in this case should be virtually impermeable because gases cannot diffuse into a metal as they can into plastic.

Factors Affecting Ingress

Three factors were tested for their possible effect on air ingress; these were the condition of the glass sealing surface, the amount of pressure used in applying the crown to the package, and the nature

TABLE II
Air Content as Determined by the Zahm Method of Beer Packages Stored for Up to 14 Weeks in Air at Room Temperature

Package[a]	*n*	Air (ml STP) Initial	Final	Change	Age (weeks)
12-oz can	54	0.40	0.44	0.04	12
12-oz NR	66	0.41	0.54	0.13*[b]	14
12-oz Ret	63	0.58	0.85	0.27*	14

[a] Packages marked NR were bottles sealed with regular commercial, twist-off closures lined with polyvinyl chloride. Packages marked Ret were sealed with regular commercial, pry-off closures lined with polyvinyl chloride.
[b] * Indicates a significant difference from zero at a 95% level of confidence using the Wilcoxon signed rank test.

TABLE III
Comparison of Crowns Lined with Polyvinyl Chloride or Aluminum Spots for the Amounts of Headspace Oxygen and Nitrogen (ml STP per 12 oz) Admitted During a One-Week Test Period[a]

Closure	Oxygen Arrival	Stored[b]	Diff.	Nitrogen Arrival	Stored[b]	Diff.
PVC	0.003	0.002	−0.001	0.081	0.158	+0.077
Al	0.004	0.004	0.000	0.091	0.094	+0.003

[a] Bottles contained beer and were sealed with regular commercial pry-off crowns.
[b] Bottled beer was stored for one week at 38° C in nitrogen (30 psig).

of the material used in the crown liner.

We tested the first of these, i.e., the effect of the glass sealing surface, by classifying returnable bottles into six categories based on three features of the bottle finish (the sealing surface). Only six categories were used in the test because not all combinations of features were found in practice. The bottles were filled with beer in the pilot plant and sealed with PVC-lined crowns. The results are shown in Table IV. All of the classes exhibited an increase in headspace nitrogen content after two weeks of storage. Classes 3 and 6, however, showed the largest and smallest increases respectively; the mean changes in headspace nitrogen contents were compared using a t test. We found a t value of 0.73 with 20 degrees of freedom. This indicates that the two classes of bottles did not significantly differ at the 95% confidence level, and by extension, that the bottle top condition did not play a major role in determining the amount of nitrogen ingress. Apparently, the PVC liner is sufficiently pliable to fill minor surface imperfections.

The pressure on the crown during application is adjusted by varying the tension of a spring in the crowner. Beer was commercially packaged in bottles sealed at three different crowner spring tensions. Bottles were analyzed for nitrogen ingress. The data in Table V show that bottles sealed with the lower spring tension (300 lb) admitted 0.14 ml of headspace nitrogen, whereas bottles sealed at the higher pressures (850 or 950 lb) admitted 0.11–0.13 ml of headspace nitrogen. Apparently, the greater amount of deformation that the higher spring tension places on the crown liner is not sufficient to produce a large difference in the amount of nitrogen admitted into the package.

The third factor tested was the liner itself. Since different manufacturers employ different liner configurations as well as possibly different liner compositions, i.e., the nature and amounts of plasticizers and lubricants in the liner, a test of crowns from different manufacturers might reveal differences in permeability. Crowns from five manufacturers were tested. Both foamed and solid liners were included in the test. Bottles of beer were commercially filled, sealed with crowns from the different manufacturers, and analyzed for their nitrogen contents at receipt and after three months of room temperature storage. The results are shown in Table VI. Crown A was a prototype not in commercial production. The column headed "Change" shows that the crowns did admit different amounts of nitrogen. Crown A admitted the least while crown D(S) admitted the most. It should be mentioned that many of the bottles sealed with crown A developed obvious leaks and were excluded from testing. A pairwise comparison was made of the crowns using BMDP7D to see if there were any statistically significant differences in the amounts of nitrogen admitted. The performance of crown A was found to be better than that of crowns D(F) and D(S) at the 99% or greater confidence level, and the performance of C(F) was also better than that of D(F) or D(S) at the 95% or greater confidence level. The mean results from the other crowns did not differ significantly at the 95% confidence level. These results indicate that design features, composition, or both do play a role in gas permeability.

TABLE IV
Average Headspace Nitrogen Contents ($n = 12$) in Six Sets of Bottles Classified by the Condition of the Bottle Finish[a]

Bottle Class[b]	Nitrogen (ml STP/12 oz) Initial	After Two Weeks	Change
1	0.136	0.250	0.114
2	0.130	0.228	0.098
3	0.150	0.232	0.082
4	0.143	0.253	0.110
5	0.144	0.240	0.096
6	0.139	0.259	0.120

[a] Bottles contained beer and were sealed with regular commercial pry-off crowns and stored in 30 psig nitrogen at 38°C.
[b] Bottle classes were based on three features of the finish (the sealing surface): the presence or absence of a ridge sometimes left by the glass mold, whether the lip (where the top surface meets the interior sidewall) was smooth or sharp or roughened, and whether the top was smooth or rough as would be caused by multiple use of the bottle. The classes were: 1 = ridge with smooth lip; 2 = ridge with sharp lip; 3 = smooth top with sharp lip; 4 = smooth top with smooth lip; 5 = rough top with rough lip; 6 = rough top with slightly rough lip.

Comparison of Experimental and Calculated Transmission Rates

If permeation is in fact the mechanism by which gases pass into the package through the crown liner, it should be possible to calculate the rate at which oxygen or nitrogen would pass through the crown liner into the package using the crown liner dimensions and published permeation data. Transmission rates for various gases through PVC and other plastics have been measured and are a function of the thickness and area of the membrane being tested, and the difference in partial pressure (the driving force for transmission) across the membrane. The permeability of a plastic is expressed as

$$P = \frac{V \times Th}{A \times t \times \Delta P} \qquad (1)$$

where V is the volume of the specified gas, Th is the thickness of the plastic membrane, A is the membrane area, t is the time of the test, and ΔP is the difference in pressure of the specified gas on either side of the membrane. A unit of measurement often quoted in the literature is the centibarrer or cB (1). It is the permeability coefficient for a specific plastic and gas at a certain temperature and is expressed as

$$1 \text{ cB} = \frac{10^{-12} \text{ cm}^3 \times \text{cm}}{\text{cm}^2 \times \text{sec} \times \text{cmHg}} \qquad (2)$$

This states that a plastic with a permeability of 1 cB will transmit 10^{-12} cm^3 of the specified gas in 1 sec through a membrane that is 1

TABLE V
The Effect of Bottle Crowner Spring Tension on the Amount of Headspace Nitrogen Admitted During a Two-Week Test Period in Nitrogen at 38°C[a]

Spring Tension[b] (lb)	Nitrogen (ml STP/12 oz) Initial	After Two Weeks	Change
300 (T)	0.272	0.412	0.140
850 (P)	0.514	0.624	0.110
850 (P)	0.374	0.505	0.131
950 (T)	0.584	0.684	0.100
950 (T)	0.522	0.645	0.123

[a] Regular commercial twist-off and pry-off closures with liners were used on beer filled packages.
[b] (T) = twist-off and (P) = pry-off.

TABLE VI
Comparison of Total Nitrogen Ingress into 12-oz Bottles of Beer Sealed with Various Supplier's Twist-Off Crowns and Stored in Air at 22°C

Supplier[a]	Nitrogen (ml STP/12 oz) Initial	After Three Months	Change	Rank[b]
A(S)	0.421	0.476	0.055	1
B(F)	0.448	0.675	0.227	4
B(S)	0.463	0.664	0.201	3
C(F)	0.472	0.579	0.107	2
D(F)	0.463	0.804	0.341	6
D(S)	0.465	0.870	0.405	7
E(F)	0.377	0.608	0.231	5

[a] F and S indicate foamed and solid liners, respectively.
[b] Crowns were ranked based on the change in nitrogen content. 1 = the least change and 7 = the most.

TABLE VII
Two-Way Taste Test Results for Beer in 12-oz Bottles Sealed with Regular Commercial Pry-Off Closures Lined with Polyvinyl Chloride and Stored for 60 Days in Air or in Nitrogen at 22°C

	Storage Condition	
Taste Test Variable	***Air***	**Nitrogen *(30 psig)***
Quality rating (0–9 scale)	4.5	4.9
Number preferred	5	12
Flavor attributed at the 75% probability level	Astringent	Smooth

cm thick, has an area of 1 cm^2, and across which the pressure difference of the specified gas is 1 cm of mercury (Hg). A typical crown has a PVC sealing ring 22 mm in diameter and 0.6 mm high. One can conceive of this ring as an open ended cylinder or tube whose exterior surface area is 0.412 cm^2. The thickness of the ring (or in our cylinder concept, the thickness of the cylinder wall) is 0.27 cm. The permeability coefficient for nitrogen in PVC at 25° C is 0.5 cB (4). The partial pressure of nitrogen in air is 59 cmHg, and the number of seconds in a day is 86,400. Upon substituting the preceding values into equation 1 above, one obtains a calculated transmission rate of 3.9×10^{-6} cm^3 of nitrogen per day. The actual amount of nitrogen transmitted into packages can be obtained from the data in Table VI. On the average, the seven different crowns admitted slightly more than 0.22 ml of total nitrogen during the three-month test period, or about 2.5×10^{-3} cm^3 per day. This value is about three orders of magnitude greater than the number calculated from equation 1. A number of factors may contribute to the discrepancy. The permeability coefficient quoted is for the pure polymer; the PVC used in crowns is in fact combined with a number of other compounds, such as plasticizers, to permit it to perform its sealing function. The permeability is likely increased by the presence of these additives. Humidity is also likely to increase permeability, and this would naturally be high inside the package. It is probable then that the discrepancy between the actual and calculated transmission rates may not be as large as first thought. However, the factors that might bring the two numbers into closer agreement are not known at this time.

Permeability and Taste

Using the experimentally determined transmission rate for nitrogen (0.0025 ml/day) and the fact that oxygen is approximately three times more permeable in PVC than nitrogen (see earlier discussion), one can calculate that 0.0018 ml of oxygen per day can get into a beer bottle stored in air at room temperature, or about 0.11 ml in two months. This translates into an additional 0.5 ml of air per 12-oz package—an amount that would certainly be unacceptable in production and one that could affect flavor. To see if beer flavor was in fact changed by the ingress of air into the bottle, a taste panel compared the flavor of bottled beer stored in air for 60 days with the flavor of the same beer stored in nitrogen. The results are shown in Table VII and indicate that 12 of 17 panelists preferred the nitrogen-stored beer. It was judged smoother than the air-stored beer package. This type of test was repeated on a number of occasions with mixed results. The nitrogen-stored beer was not always the preferred product. Further investigations into the effect of permeability on taste are required.

CONCLUSIONS

Even though the pressure inside a beer bottle is greater than atmospheric pressure, oxygen and nitrogen from the air can pass into the package through a PVC-lined crown. The reason for this ingress is the difference in partial pressure of the permeating gases between the inside and the outside of the package and the fact that the PVC liner acts as a semipermeable membrane. The phenomenon does not occur in bottles sealed with aluminum spot-lined crowns or in cans. Ingress does not appear to be measurably influenced by the condition of the glass sealing surface or the amount of pressure used in applying the crown to the bottle. Different types of liners transmit different amounts of gas. Maintaining the bottled beer at a low temperature reduces permeability.

Changing the configuration of the liner to change the diffusion path or incorporating less permeable constituents in the liner may reduce permeability. Flavor is probably affected by the permeation of oxygen into the package, but this is an area which requires more study.

LITERATURE CITED

1. American Society for Testing and Materials. 1982 Annual Book of ASTM Standards, Part 35. Method D1434-75. The Society: Philadelphia, PA, 1982.
2. Amini, M. A., and Morrow, D. R. *Package Eng.* 21:37, 1976.
3. Cooper, W. C. *Brew. Dig.* 26:45, 1951.
4. Shur. Y. J., and Ranby, B. *J. Appl. Polym. Sci.* 20:3121, 1976.
5. Snedecor, G. W., and Cochran, W. G. Pages 125–130 in: Statistical Methods, 6th ed. The Iowa State University Press: Ames, IA, 1967.
6. Wisk, T. J., and Siebert, K. J. *J. Am. Soc. Brew. Chem.* 44:72, 1986.
7. Zahm and Nagel Co. Zahm Practical Testing Instrument Manual, 11th ed. Zahm and Nagel Co.: Buffalo, NY.

[Received August 8, 1986. Accepted September 30, 1986.]