# Use of Oxygen Absorbers in Dry Pack Canning

## Abstract

Albert E. Purcell, Theodore C. Barber, and John Hal Johnson.

Benson Quality Assurance Laboratory
Department of Food Science and Nutrition
Brigham Young University, Provo, Utah

A study of the effectiveness of oxygen-absorbing packets, Ageless Z300, was conducted. The packets were effective even in empty No. 10 cans for reducing the oxygen levels to near zero. The packets have greater than claimed capacity, thus they can withstand a little abuse before use. Smaller packets with a capacity calculated on "dead air" volume of foods may be just as effective as the Z300 but would have less resistance to abuse.

Objective: The objective of this study is to test the effectiveness of oxygen absorbing packets in removing oxygen from inside #10 cans filled with dried milk or macaroni.

## Materials and Methods

Cans: Standard #10 cans which are used for cannery dry pack, with lids.

Milk: Dried Deseret Brand nonfat dry milk, the same as is used in cannery dry pack operations.

Macaroni: Deseret Brand elbow macaroni, the same as is used for cannery dry pack.

Oxygen scavengers: Ageless Z300E, Mitsubishi Corp.

Gas sampler: A sampler was designed based on a commercial gas sampler for aerosol cans. The design allows a sample of gas to be taken through the lid of a #10 can. Details of the sampler may be obtained from the Benson Quality Assurance Laboratory, Brigham Young University, Provo, Utah, 84602.

Sample syringe: A 1 ml Pressure-Lok Series A gas sampling syringe (Precision Sampling Corp., Baton Rouge, LA.) was used to penetrate the can for collection and delivery of the sample to the gas chromatograph.

Gas Chromatograph: Packard Dual Column, model A was equipped with Model 886 T.C. Detector, TC Detector Power Supply Model 839, Deviation Temperature Controller Model 873, Coiled Column Air Oven Model 804, and a Dual Flow Controller Model 824.

Columns: Molecular Sieve 5A for separation of $O_2$ and $N_2$ and PoraPaKQ for separation of $CO_2$.

Helium at 46 ml/min was the carrier gas. Eluted components were detected by a thermal conductivity detector. Injection port temperature was 40°C, column temperature was 40°C and detector temperature was 200 °C. Signals from the detector were recorded on a Hewlett-Packard (3390A) integrator which automatically integrated peak area and calculated

percent of area under each peak. Peak area was proportional to the amount of each gas detected.

**Preparation of samples:** There were 9 treatments with 6 cans each. Six cans were sealed with air at the site of perparation designated "Blank" (Table 1). These cans provided samples for calibrating the gas chromatograph.

Six (6) samples contained air with one fresh oxygen absorbing packet (Z300) which had less than 5 min. exposure between opening the factory package and sealing the can. These were designated Fresh. Six (6) samples contained air and one Z300 packet exposed to air for four hours on a laboratory table with at least 25mm distance from any other packet, designated "X". Six (6) cans contained 1517g dried milk, designated MilkO. Six cans contained 1517g dried milk and one fresh packet, designated Milk fresh. Six cans contained 1517g of dried milk and one exposed oxygen packet, designated MilkX. Six cans contained 1172g macaroni, designated MacO. Six cans contained 1172g macaroni and one fresh oxygen packet, designated Mac Fresh and six cans contained 1172g macaroni and one exposed oxygen packet (MacX). The cans were sealed and stored at 19-21°C for 4 hours, 7 days and 14 days before analysis.

Estimating the amount of air in cans:

An empty #10 can holds 3078 ml of water when filled to the bottom of the top lid. The same cans will hold 1785g of dried milk or 1440g of macaroni when filled to the top lid. After cans were filled with a product the can was weighed and filled to volume with hexane. After the hexane had displaced air entrapped in the product the can, were weighed

again to determine the weight of hexane. Weight of hexane was multiplied by density .6584 g/ml to determine volume of the entrapped air. Volume of the can minus volume of hexane was used as a measure of the total volume of the product. It was calculated that the density of dried milk was 1.27 g per ml and was 0.7465 g/ml for macaroni. This figure includes the packing factor. Although macaroni will sink in water, suggesting a density above 1.00, the packing efficiency is low, because of the curvature and hollow center.

Results and discussion

The integrator data from the gas chromatograph gave % of oxygen and % nitrogen in each sample (Table 2). The absolute amount of each gas in the can may be estimated from can fill, "dead" space, and residual vacuum. When all of the oxygen is removed from an empty can residual vacuum will be near to 78% of the atmospheric pressure at the time the cans were sealed because about 21% of the air is oxygen. Percent of each gas allows a more direct comparison between treatments than calculated amounts would.

At 48 hours a fresh packet sealed in an empty can reduced residual oxygen to a measured 1.63%, indicating the packet absorbed 589 ml $O_2$ at standard temperature and pressure (STP), i.e. 760mm mercury and O° C. The exposed packets absorbed 542 ml at STP leaving 3.2% or oxygen. The Z300 packets are claimed to absorb 300 ml $O_2$ at STP, thus even the packets exposed for 4 hours exceeded claimed performance at 48 hours in the sealed cans. At one and two weeks fresh an exposed packet decreased oxygen levels to less than 1%. The amount of milk an macaroni used throughout this test were 15% and 18% less, respectively, than a full can. This left more oxygen in the cans than would be present in normal "dry pack".

At no time did the % oxygen in the cans drop to 1%. Residual oxygen in the sampling device could account for no more than .000029% oxygen. Design of the syringe precluded entrance of air after the sample was taken.

Chemical equilibrium in the reaction $Fe_2 + O_3 \rightleftharpoons Fe_2O_3$ is such that there would be no measurable oxygen left.

Nitrogen samples were collected in the syringe from a flowing stream of nitrogen from a tank of pure nitrogen. When introduced into the gas chromatograph, there was 0.13% oxygen, indicating that the zero line of the gas chromatograph is near zero and about 1.0% oxygen cannot be explained by sampling error.

The only explanation that seemed tenable was that the chromatograph was measuring something other than oxygen.

As a further check for sampling error 0.5 ml samples were taken and injected into the gas chromatograph. Dead space in the sampling and injection should be constant, thus the % of oxygen would double when half the volume is injected. The percent of oxygen remained constant, essentially eliminating sampling as the source of oxygen.

Handbooks[1] list 0.93% argon by volume as a normal constituent of air. Argon would not be detected by oxygen electrodes nor chemical methods. The molecular weight of argon is sufficiently different from oxygen that it was not expected to interfere with oxygen on the gas chromatograph. A tank of argon was available and the syringe was filled in a flowing stream of argon. When injected into the gas chromatograph, argon completely covered the oxygen peak. When the data were corrected by subtracting 0.93% from each

---

[1]Handbook of Chemistry and Physics, Large. Sandusky Ohio: Handbook Publishers, Inc. 1939:21

determination it appeared that oxygen levels were near zero. If percent weight of argon (1.24%) were used, some levels were below zero. The apparent slight residual oxygen may be the result of diffusion equilibrium. At two weeks the mean oxygen content in the cans was still decreasing, i.e. .46%, .42%, .34%.

The oxygen level in the cans containing food was not significantly different between a fresh packet and an exposed packet. This is because cans containing food contained less air volume hence less oxygen than the empty cans, 3078 ml air per empty can, 684 ml air in macaroni and 325 ml in milk.

No evidence of oxygen uptake by the food was found. Oxygen will obviously be taken up by the food if the food becomes rancid but the methods used were not sensitive enough to detect the amount used by the food in so short a time.

Carbon dioxide content of head space gases were measured. No carbon dioxide was found in any sample containing an oxygen absorbing packet. The drying agent in the packets would absorb carbon dioxide. Carbon dioxide in cans not containing a packet, i.e. Mac O and Milk O did not show any increase during the test period. This is consistent with the absence of detectable oxygen uptake by the foods.

Conclusions:

Oxygen absorbing packets are effective in reducing oxygen contents in sealed cans. The Ageless Z300 packet has a greater than claimed capacity for absorbing oxygen. Packets

**TABLE 2: OXYGEN AND NITROGEN CONTENT OF SAMPLES AT THREE DIFFERENT TIMES**

| | % OF $O_2$ | | | % OF $N_2$ | | |
|---|---|---|---|---|---|---|
| Sample | 48 hours | 1 week | 2 weeks | 48 hours | 1 week | 2 weeks |
| Fresh | 0.70 | 0.42 | 0.43 | 98.36 | 98.65 | 98.65 |
| X | 2.27 | 0.40 | 0.9 | 98.74 | 98.67 | 98.55 |
| Mac O | 20.05 | 20.18 | 19.89 | 79.11 | 78.81 | 79.19 |
| Mac X | 0.42 | 0.42 | 0.42 | 98.64 | 98.20 | 98.66 |
| Mac Fresh | 0.45 | 0.41 | 0.41 | 98.63 | 98.66 | 98.65 |
| Milk O | 20.33 | 19.99 | 20.14 | 78.72 | 79.07 | 78.99 |
| Milk X | 0.50 | 0.43 | 0.27 | 98.57 | 98.64 | 98.62 |
| Milk Fresh | 0.48 | 0.44 | 0.43 | 98.59 | 98.63 | 99.27 |
| | 0.46 | 0.42 | 0.34 | | | |

abused by 4 hour-exposure-to-air still exceed claimed capacity. It may be economical to use smaller packets based on the dead air volume instead of can volume. Smaller packets would have less tolerance for abuse and personnel would need to be more diligent in to predict. Microorganisms range from aerobic to anaerobic thus no unqualified statement can be made. The energy requirements of aerobic bacteria are met by reactions between oxygen and more than one other molecule. This makes bacterial energy a higher order of reaction than rancidity. Thus the rate of bacterial aerobic reaction would be more seriously retards than rancidity. These matters are not of practical importance because the products to be canned should be too dry to support microbial growth. Insects are aerobic and would like-wise suffer retardation of activity. No comprehensive statement can be made about irreversible activation or death of insects. As long as the oxygen level remains low, insect activity will be lower by at least the square root of oxygen content. In a practical sense, these packets are effective in stopping insect activity. USDA does not recognize any method except disintegration as effective for completely killing insect eggs.

To: Dean Eliason

From: Albert E. Purcell

Subject: Your letter and research proposal re: oxygen scavengers, 25 February 1993.

The proposal title and objective are straight forward and will be covered by the experimental design. Objective No. 3 was necessary to determine what size packet would be needed for removing oxygen from products in a #10 can.

Objective 4 will not be decided by the proposed research, but I believe we can, with high confidence, answer some of the questions.

A. Without doubt elimination or large reduction of oxygen will decrease the severity of flavor and delay the level of detection according to the following equation.

$$R_F = \frac{1}{\text{anti log}\left(\log 2x \frac{C_O}{C_F}\right)} \times R_O$$

$R_O$ = original rate of oxidation
$R_F$ = final rate of oxidation
$C_O$ = original oxygen concentration
$C_F$ = final concentration of oxygen

Shelf life will depend upon how much "off flavor" the user or taster can stand. Thus, shelf life is a subjective determination which must be established by panel consensus.

B. I have not seen the blue clip for resealing the packets. We can measure that on another test. Knowing that the manufacturer enjoys repeat customers, I would guess the clip, when properly used, will be reasonably effective.

C. I have only the manufactures suggestion that packets in an unopened bag will be stable for several months. We can determine this but it would be a long term storage study and would require a large number of samples because we could not test any packet without opening the bag.

I think the bags are made of mylar. If this is the case, and if there are no flaws or holes nor leaks at the seams, it would take a couple of millennia for enough oxygen to decades

diffuse though the mylar to seriously reduce the capacity of the packets. I imagine that there would be lower probality of leaks into a sealed can.

External temperature would have a small effect on the packets if ample oxygen were available. At any level of oxygen the shelf life of the packets would increase by a factor of 1.07 for every 40°F decrease in storage temperature. Diffusion to the chemical inside the packet will be limiting. High humidity will definitely use up the packets but I think it will be easier to protect the packets from oxygen than from water. The packets are not transparent, thus I would expect no effect of light. Because the rate of diffusion is limiting, light activation of oxygen would have no effect. The active ingredient in the packet is elemental iron, therefore there will be no molecular "break down", no molecular rearrangements nor intermolecular actions. This is much, much different than a food stuff with its myriad molecular species.

D. Carbon dioxide can react with food molecules and add off flavors, which some people can detect. I know of two such people. Carbon dioxide will prevent rancidity only to the degree that it will dilute oxygen. If these oxygen scavengers work as advertized they will get the oxygen quite a bit lower than can be accomplished by displacement with carbon dioxide. Carbon dioxide above 3% becomes a respiratory toxin, thus with even modest displacement of oxygen, carbon dioxide will inhibit or kill insects and their eggs. Carbon dioxide is a more potent fumigant than oxygen scavengers.

I hope I have provided adequate answers to the question raised in paragraph 4 of the proposal. I am awaiting arrival of oxygen packets to begin this work. I will have to schedule with the Lindon Cannery and Dr. Darrell Webber for the use of his gas chromatograph. How important is it to you that we follow the 2 day, 1 week, and 2 week schedule? The 2 day schedule will be particularly hard because analysis will take most of 2 days for every sampling period.

cc: John Hal Johnson