50

238

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Observations on the Gases in Sealed Flexible Packages of Meat Products

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Meat Products in sealed plastic packages are now distributed on a large scale in a number of countries, and increasing interest is being shown in the acceptable shelf life of such products. The composition of the gas inside the package is clearly an important factor governing the types of micro-organisms in the product and their speed of multiplication (Ingram 1962). In this paper we attempt to assess the amount and composition of the gas in cured meats packed in a variety of plastic films.

In commercial production a vacuum gauge is attached to the vacuum chamber in which the package is heat sealed and these gaugos normally register a high degree of vacuum, often 99% or greater. There is, therefore, a tendency to regard the resulting packages as being virtually air free. This is, however, by no means the case, and several reasons can be advanced to explain why a plastic pouch sealed under vacuum in a commercial production machine is bound to contain appreciable amounts of oxygen.

In the first place the actual time of exposure to vacuum is very short; even at the modest speed of 30 packages per minute the maximum vacuum is not operating for more than about 0.5 seconds. Consequently, there is little time for air entrapped inside the product or between slices of meat to be removed. Furthermore, if this operation is seen through an observation window, it is usual to find that the sudden lowering of atmospheric pressure causes the pouch to swell markedly and the seal may be formed while the pouch is in an inflated condition. On restoring atmospheric pressure to the outside of the pouch it collapses thus compressing the entrapped air. Indeed it may be said that, unless the package or its contents show some degree of rigidity, the pressure inside the packet is bound to be equal to that of the external atmosphere. Yet another distinction between vacuum packaging in plastic films and the corresponding operation in metal cans is, that few plastic films are entirely impermeable to oxygen. Thus, even if the sealing operation were carried out perfectly, subsequent ingress of oxygen would occur through the film.

EXPERIMENTAL WORK

240

1 Experiments using Normal Gas Analysis Equipment (Series 1)

In 1958 experiments were carried out jointly with the Laboratory of the British Oxygen Company using the following materials:-

(a) Bacon - Sliced smoked back bacon

(b) Pouches - Polythene coated regenerated cellulose film with an outer coating of nitro-cellulose lacquer, (MSADT/poly).

The pouches were sealed in a normal commercial vacuum heat sealing machine and were examined immediately after packing, after storage for 7 and 14 days at 32-34°F (0 - 1°C) and also after storage for 7 and 14 days at 65-70°F (18 - 21°C).

Gas Sampling Method

The pouches were placed separately in a vacuum desiccator (D) which was subjected to a high vacuum ($c.10^{-2}$ mm.Hg.) This caused the pouches to swell and become tightly distended. The pouches were then burst by manipulating a mounted razor blade and a measured sample of the gas transferred by means of a three-way tap (T) and a mercury filled bulb (B) and levelling tube (L) (Fig. 1) into a Bone and Wheeler apparatus. The sample of entrained gas was analysed volumetrically by liquid absorption for oxygen and carbon dioxide and the remainder was considered to be nitrogen.

Calculations of Gas Volumes

By extracting successive known fractions of the combined desiccator plus bulb volume, the quantity of gas taken into tbe Bone and Wheeler apparatus can be used to calculate back the original volume of gas in the pouch.

Results

See Table 1.

2 Experiments using Gas Chromatographic Techniques (Series 2)

Liquid absorption gas analysis requires a sufficient volume of sample gas to allow accurate volumetric assessment. The technique of gas chromatography permits much smaller volumes

to be measured. Application of the principle of separation of gaseous constituents on an absorptive column with subsequent detection and estimation of the components uses quantities of the order of 100 µl, of pouch gases. A sampling procedure can be devised where the gases in a packet of product can be diluted with a suitable gas, mixed and sampled in ml. quantity.

241

In the Packaging Laboratory of T. Wall and Sons (Meat and Handy Foods) Ltd., recent experimental work has thrown new light on the atmosphere inside sealed "air-free" packs of curod meat products. The apparatus and technique are essentially those described by Bishop and Humphrey (1962).

Materials

(a) Products

(i) Sliced Back Bacon - Wiltshire Cure-Smoked

(ii) Sliced Cooked Ham

(b) Films

(i) Low Density Polythene (300 gauge)

(ii) Polythene coated regenerated cellulose film with a nitro-cellulose outer lacquer (MSADT/poly)

(iii) Polythene coated regenerated cellulose film with a PVDC polymer outer coating (MXDT/poly)

(iv) Paper/polythene/Aluminium foil/polythene, composite

The products were packed in the various films in pouch form and sealed in a Souvidex Vacuum Heat Sealing Machine Model J.380. This machine was used in preference to a Factory Production Model for ease of change of sealing characteristic to accommodate the various films.

The packed meats were stored at a constant temperature of 68°F (20°C). Packs were taken for gas analysis immediately after packing, and after one, four, eight and sixteen days storage for bacon and after two, four and eight days storage for the ham.

Gas Sampling and Estimation

The procedure entailed introducing 20 ml. of argon into the pack through a rubber patch stuck to the face of the pouch, via a hypodermic syringe. By subjecting the pack to a negative pressure and ballooning it slightly an adequate mixing of the diluent gas and the pouch gas could be obtained. Sampling the mixture at atmospheric pressure was made using a 1 ml. hypodermic syringe, 30 minutes after dilution.

242

The detecting and estimating equipment is shown diagramatically in Fig. 2. The 1 ml. of mixed gases is injected through a synthetic rubber diaphragm (D) into the stream of argon, controlled by a flowmeter (F), supplying the particular column being used. For oxygen and nitrogen a molecular sieve (M) material (a modified Zeolite, 5A, 40 - 60 mesh fraction) is used supported in a copper tube. A parallel silica gel column (S) separates carbon dioxide. We employ argon rather than helium as a carrier gas and diluent to reduce any tendency to lose gas through the film materials during mixing. Detection of the small quantities of other gases in the argon stream in this equipment utilises the katharometer technique (K).

In this method use is made of the change in thermal conductivity of the carrier gas caused by the emergent trace gases. A detector thermistor in the carrier gas stream has a small current passing through it producing heat which is dissipated by the carrier gas. In the thermal equilibrium state, the resistance of this thermistor is balanced against a reference thermister in the parallel gas stream, and the bridge circuit (B). The trace gases separated on the column affect the thermal character of the detector thermistor and throw the bridge circuit out of balance.

This out-of-balance current is amplified (A) and fed to a pen recorder (R) and provides a permanent record of the quantity of emergent trace gas. Calibration of the recorder is made using an air sample for the molecular sieve column separation of nitrogen and oxygen. For the calibration of the silica gel column separation of carbon dioxide we use pure carbon dioxide diluted with argon. The sensitivity of the apparatus requires operation at a constant temperature and we employ a room at $68^{\circ}F$ ($20^{\circ}C$), since the apparatus is not thermostatically controlled.

For the purpose of these experiments the peak of the tracing in relation to the base line has been taken as a measure of the volume of the trace gases separated on the columns. While this is not strictly precise (the area under the trace is more correct) it allows a rapid estimation for comparative work.

Results

See Figs. 3 and 4, and Table 2.

243

COMPARISON OF THE RESULTS OF THE TWO ANALYTICAL METHODS

The essential difference between the methods described lies in the manner of sampling. In the earlier method the gas in the packs was withdrawn by the application of high vacuum and this could have caused an artefact. Some carbon dioxide could have been extracted from the meat, leading to an over estimate of this component of the pouch gases. The recent technique using argon dilution at atmospheric pressure followed by gentle manipulation and withdrawal of the sample, overcame this problem to some extent.

That carbon dioxide had been extracted from the meat in the Series 1 experiments is indicated by comparison of the Day 0 figures of gas volume and percentage composition, for bacon packed in MSADT/poly, of the two Series as follows:

	Volume of Gas in Pouch	% Composition		
	ml	CO_2	O_2	N_2
Series 1 (b)	3.8	71.5	3.7	24.8
Series 2	2.07	20.3	14.5	65.2

It can be argued that the excess gas volume (1.73 ml) is due to carbon dioxide extracted in the Series 1 method. Recalculating the percentage composition of the Series 2 figures to include this extra carbon dioxide, the composition would be as follows: - 56.6% CO_2, 7.9% O_2, 35.5% N_2, which is more of the order of the figures quoted in Series 1. It should be noted that the amount of carbon dioxide extracted, in Series 1, varies considerably from sample to sample as can be seen from comparison of the Day 0 figures for storage type (a) and storage type (b), (see Table 1).

Discussion

In Series 1 the difference in oxygen level in the pouches stored at different temperatures is presumably related to the state of dynamic equilibrium in these pouches. Oxygen is continuously permeating the film and its seals and is balanced by the uptake of oxygen by the meat. The temperature rise effect on oxygen uptake by meat is fairly marked and presumably exceeds the effect of the temperature rise on the permeability of the film to oxygen.

In Series 2 from the graphs it will be seen that initially with both ham and bacon the percentages of oxygen in the packs are high, 12-20%, but that in the case of the polythene packs the oxygen percentage at the start is nearer 30%.

244

Carbon dioxide at the start of the storage period was high for bacon 9-28% but lower in the case of ham, about 5%. The bacon carbon dioxide level is much higher than can be explained on solubility data. The proportions of the three gases in equilibrium with a 5% solution of sodium chloride at 0°C (comparable with the salt in solution in the bacon lean) are 61.1% N_2, 35.8% O_2, 3.1% CO_2. Similar results are obtained when equilibrium concentrations are calculated for biological fluids or for lard.

This infers that in the bacon carbon dioxide is loosely absorbed and may be liberated even with the argon dilution technique.

In Series 2, as storage progressed, two main factors began to play their parts:

(i) The permeability of the films to the three gases

(ii) The growth of micro-flora and the production of carbon dioxide by them.

The order of permeability of the films to oxygen is as follows:

(i) Polythene the highest

(ii) MSADT/poly

(iii) MXDT/poly

(iv) Aluminium foil laminate, the lowest

The highly permeable polythene film apparently showed an increase in oxygen content during the first day followed by a gradual decrease, presumably as the uptake of oxygen by micro-organisms and the meat itself began to take effect. The carbon dioxide content showed an inverse pattern.

It is interesting to note that the carbon dioxide permeabilities of the four films are in the same order as the oxygen permeabilities but there is a sharp demarcation between MSADT/poly and MXDT/poly. This could account for the differences in carbon dioxide found in bacons packed in these two films in the early and final stages of storage.

From Table 2, the quantities of gases in the various packs during storage, it will be noted that there is apparently a decrease in total volume between Days 0 and 1 in the case of bacon in the less permeable films. The decrease in oxygen volume cannot account for this difference alone, and it is difficult to explain how the nitrogen could have decreased.

The changes in gas composition inside packs with different films during storage, show that we must regard the packs as being in a state of dynamic balance.

If we assume that the lowest possible oxygen content and highest carbon dioxide content will contribute towards extended shelf-life, both in appearance and in microbiological condition, then the better pair of films of the four tested are the MXDT/poly and the aluminium foil laminate. After four days storage, bacon packed in these films showed negligible oxygen, 51-55% carbon dioxide and 44-48% nitrogen.

The present study did not include any bacteriological examination but it seems likely that these conditions would increase the inhibitory effect of curing salts and smoke on the growth of many types of micro-organisms.

SUMMARY

The gas contents of flexible packages of meat products have been examined both by classical liquid absorption and by gas-solid chromatography techniques.

Evidence is presented to show the marked influence of the four types of film on gas composition during storage of cured meats at 68°F (20°C).

ACKNOWLEDGMENT

We are grateful to the British Oxygen Company Ltd., for designing and carrying out the analytical procedure described in Series 1, and for permission to reproduce the results.

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J. appl. Bact. 25 (2) 259-281

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TABLE 1

Volume and Composition of Gases in Bacon Pouches Analysed by a Volumetric Absorption Method (Series 1)

Bacon stored at (a) 32-34°F (0-1°C)
(b) 65-70°F (18-21°C)

Storage Type	Storage Days	Total Volume (ml)	% Composition		
			Oxygen	Nitrogen	Carbon Dioxide
a	0	2.4	9.3	41.5	49.2
a	1	6.6	7.5	58.2	34.3
a	7	4.5 (av. 2)	7.3	51.5	41.2
a	14	2.8 (av. 2)	10.0	54.5	35.5
b	0	3.8 (av. 2)	3.7	24.8	71.5
b	7	4.3 (av. 2)	5.2	37.6	57.2
b	14	4.1 (av. 2)	2.8	31.3	65.9

TABLE 2

Average Total Volume (mls) of Gases in Packs, in Different Films Stored at 68°F (20°C). (Series 2)

Day	Polythene		MSADT/poly		MXDT/poly		Al/poly laminate	
	Bacon	Ham	Bacon	Ham	Bacon	Ham	Bacon	Ham
0	2.61	2.52	2.07	1.78	1.91	1.78	1.61	1.75
1	2.40	-	0.86	-	1.07	-	0.86	-
2	-	3.02	-	1.42	-	1.26	-	1.08
4	2.50	2.27	1.30	0.92	1.35	1.40	[illegible]	1.27
8	-	4.67	1.88	2.58	2.21	1.77	1.61	1.74
16	-	-	0.52	-	2.95	-	2.50	-

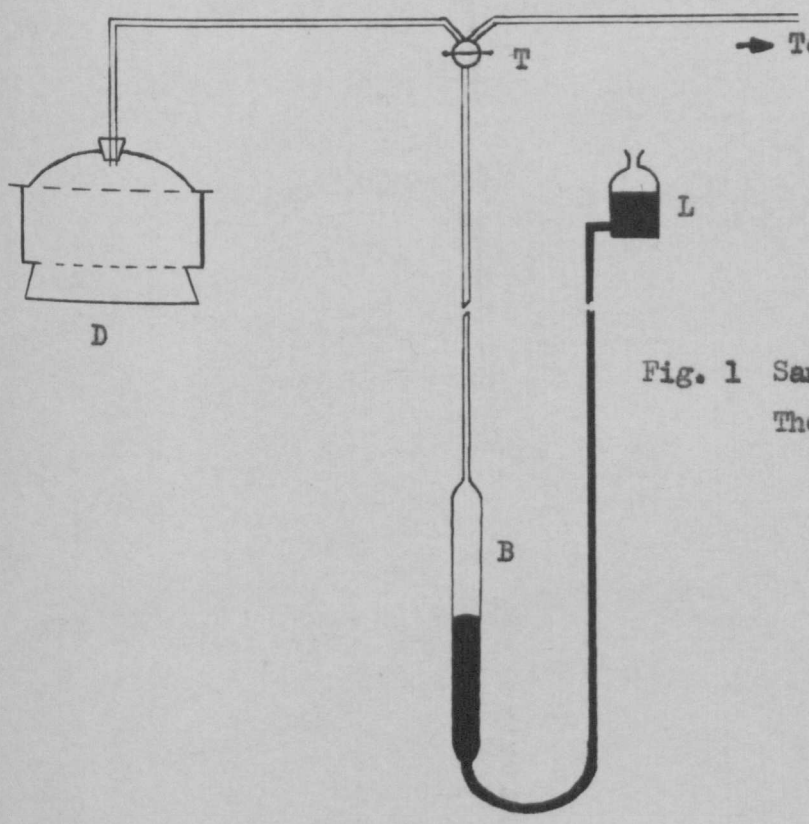


Fig. 1 Sampling Device designed by
The British Oxygen Company Ltd.

Fig. 2 Diagram of Gas-Solid Chromatography
Equipment.

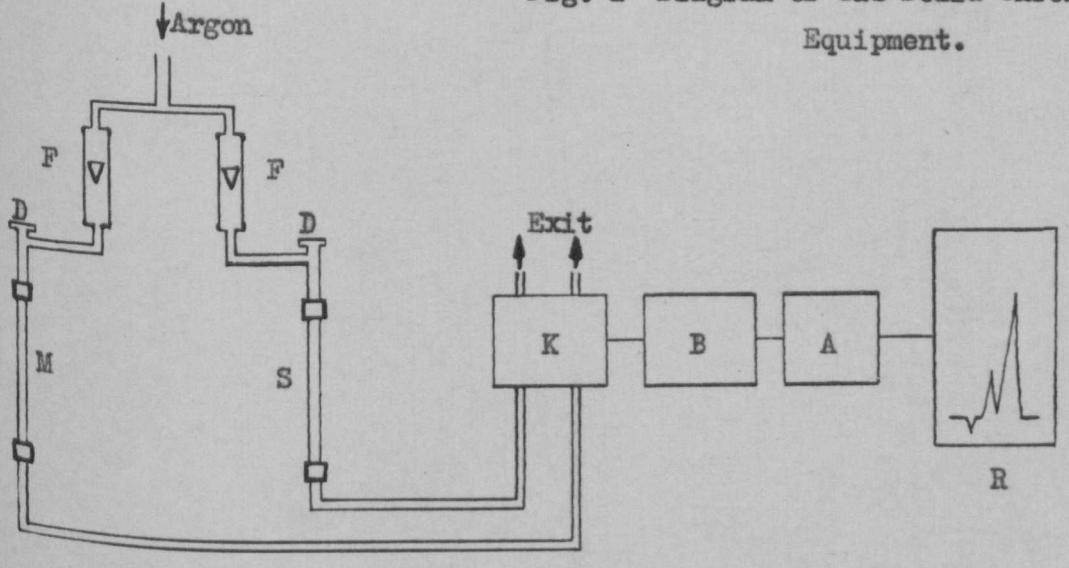


Fig. 3 % Composition of Gases in Packs of Bacon Stored at 68°F (20°C).

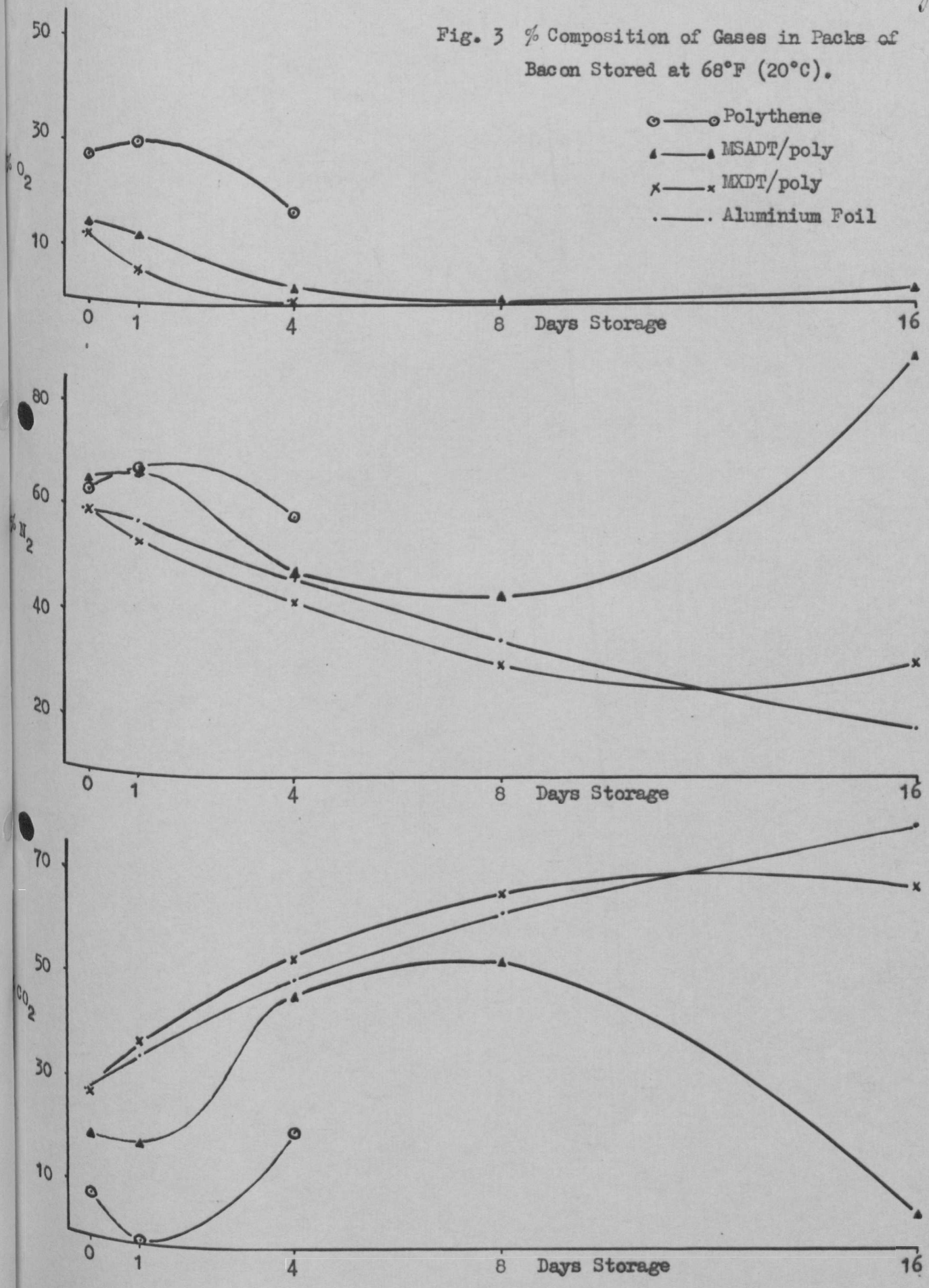
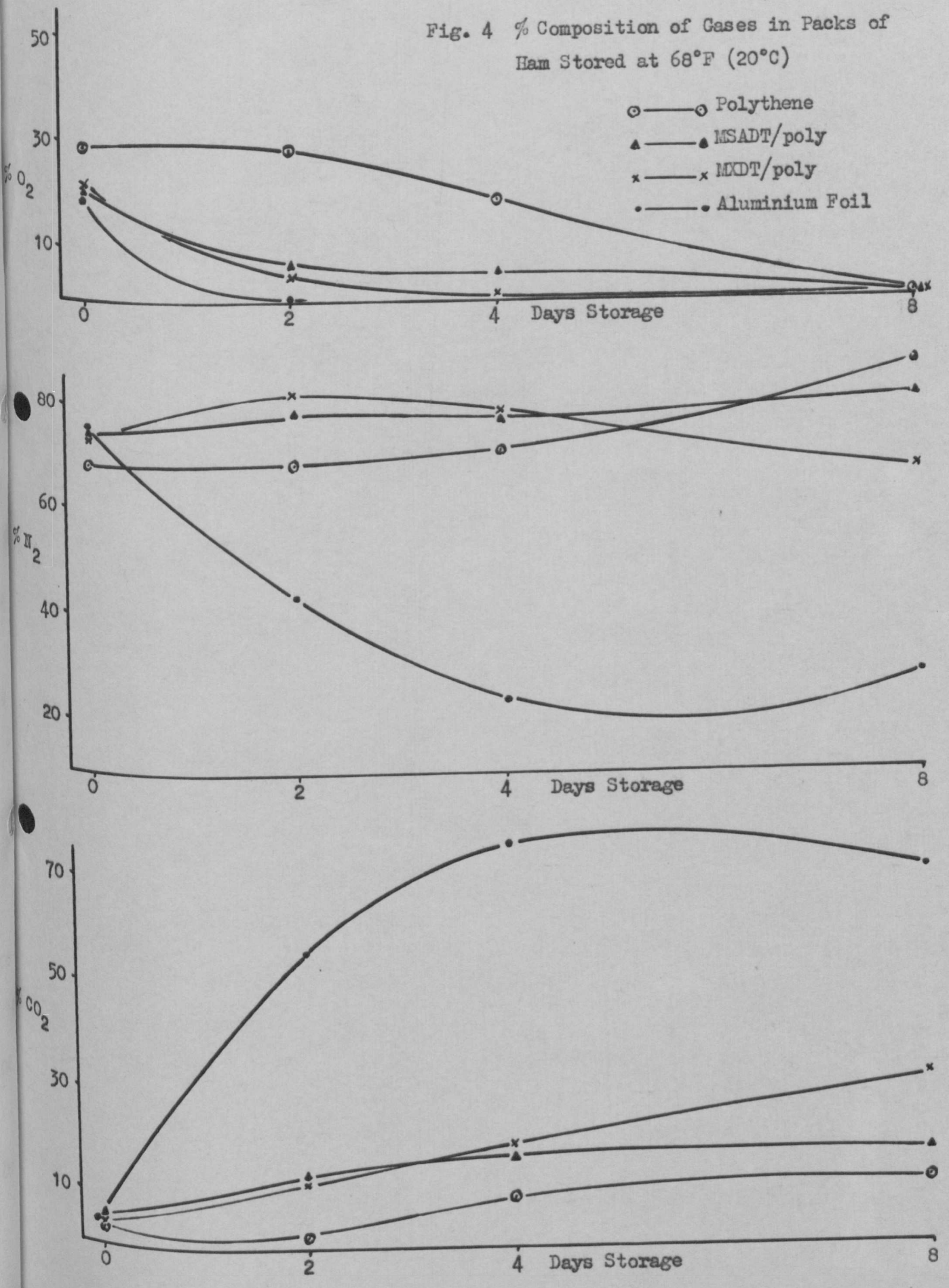


Fig. 4 % Composition of Cases in Packs of Ham Stored at 68°F (20°C)



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OBSERVATIONS SUR LES GAZ DANS LES PAQUETS FLEXIBLES SOUDES CONTENANT DES CHARCUTERIES

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RESUME

Les gaz contenu dans les paquets flexibles de charcuteries ont été examinés par la methode classique de l'absorption volumétrique et celle de la chromatographie des gaz/ solide.

Des tranches de jambon et de Bacon fumé, emballées sous vide dans quatre genres differents de pochettes ont été stockés à une température de 20°C pendant 8 jours pour le jambon et 16 jours pour le Bacon.

L'évidence presentée indique que le Bacon emballé entre deux feuilles contresoudées de chlorure-iden de Polyvinyle copolymère/cellulose régénérée/polyéthylène et d'autre part entre deux feuilles d'aluminium couvert de polyéthylène, avait après quatre jours une atmosphère gazeuse composée d'une quantitée negligeable d'oxygène, de 51-55% de bioxyde de carbone et de 44-48% de nitrogène.

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