

- (7) Johnson, G. M., *J. Assoc. Offic. Agr. Chemists* **17**, 451-3 (1934).
- (8) Lugg, G. A., Wright, A. S., *Australia, Dept. Supply, Defence Research Labs., Circ.* **14**, 1-48 (1953).
- (9) Mapes, D. A., Shrader, S. A., *J. Agr. Food Chem.* **2**, 202-3 (1954).
- (10) Webb, F. J., Kay, K. K., Nichol, W. E., *J. Ind. Hyg. Toxicol.* **27**, 249-55 (1954).
- (11) Wechsler, H., *J. Polymer Sci.* **11**, 233 (1953).
- (12) Winteringham, F. P. W., *J. Soc. Chem. Ind. (London)* **61**, 186-7 (1942).
- (13) Zincke, Th., *Ann. Chem. Liebigs* **330**, 367 (1904).

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MEAT COLOR RETENTION

Effects of Package Type, Irradiation, and Treatment with Aureomycin on Redness of Vacuum-Packaged Beef Cuts

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Redness of fresh beef samples, vacuum-packaged in cans and in film packages, was measured. Samples in cans with small head space had better red color than those in any film-type package. Of the film materials, a coated polyethylene gave the best red-color preservation. Aureomycin treatment of samples prior to packaging was detrimental to red-color retention. Irradiation at a 500,000-rep. level was detrimental to the red color of samples in cans or film packages.

PREPACKAGED SELF-SERVICE MEAT has largely replaced individual butcher service in the store. There is a problem in maintaining good color in meat in self-service distribution.

Oxygenated myoglobin gives fresh raw meat its bright red color; hence prepackagers maintained conditions that they believed would produce and retain oxymyoglobin.

According to researchers, in certain chemical systems, metmyoglobin, having grayish brown color, is produced from reduced myoglobin at a rapid rate when the partial pressure of oxygen in the surrounding atmosphere is about 1 mm. of mercury. The rate of metmyoglobin formation decreases with increasing partial pressure of oxygen until the value of 30 mm. of partial pressure of oxygen is reached. At this point, the rate becomes constant up to 80 mm. of partial pressure of oxygen. At and above this oxygen tension, reduced myoglobin is converted to oxymyoglobin, which is stable as long as the surrounding atmosphere contains free oxygen at a pressure in excess of 80 mm. of mercury.

Prepackagers concluded that the only way to obtain a satisfactory color in prepackaged meat is to maintain free oxygen at a pressure of at least 80 mm. in contact with the meat. They sought a packaging film which had a high transmission rate of oxygen, to allow oxygen of the air to have access to the meat, and a low transmission rate for moisture, to prevent dehydration. Cellophane, coated on one side with a moisture-resistant material, answered the purpose best when packaged under normal atmospheric con-

ditions. According to Landrock and Wallace (8) and others, the cellophane, used in this manner, is saturated with water from the meat, permitting it to transmit oxygen, but the coating on the outside prevents the water from getting out—to a degree.

Results reported herein point strongly to the desirability of following a course diametrically opposed to that which is now in use.

In the currently used package, oxygen can reach the meat from the atmosphere, resulting in the retention of a pleasing bright red color or "bloom" in the meat after packaging. Within 48 hours, however, this bloom is lost and a discoloration, due to the change of the red pigments (myoglobin and oxymyoglobin) to the brown pigment (metmyoglobin), as described by Brooks (3) and George and Stratmann (5), has occurred. This brown discoloration is unacceptable to the consumer and necessitates the packaging of meat in the individual store as loss of redness would occur during transportation from a central point to retail outlets. Meat, packaged after slaughter and hanging, distributed to retail stores from a central point would result in greater economy and efficiency in distribution to the consumer.

In 1949, an investigation (1, 4, 10-12) was started by the Departments of Animal Husbandry and Food Technology, N. J. Agricultural Experiment Station, to find a technique of prepackaging which would permit centralized prepackaging of fresh meat. The project was concentrated on vacuum packaging throughout, with the basic control package being tin-plate cans

hermetically sealed under high vacuum.

Fresh meat packed under vacuum lost its red color very quickly and the higher the vacuum and the storage temperature, the higher the rate of color change. However, as vacuum-packed meat was held, red color returned at a variable rate, which was generally low. Under the conditions established in the experiments, 2 weeks or longer were needed for a good color to return. Accelerating the return of red color to meat in cans and finding a transparent film in which the action could be duplicated were the next steps.

In the earliest work, cans were used in which only 20% or less of the volume of the can was occupied by the sample. As a perfect vacuum in the cans could not be obtained, reducing the size of the can in comparison to the volume of the sample (40% of can volume) brought about an accelerated return of red color. Later a can was adopted in which the sample occupied at least 90% of the can volume. In this can, with high vacuum, the initial loss of color is greatly reduced and good red color returns in from 2 to 4 days after packaging.

In the above project and in studies by others, meat has been packaged experimentally in materials differing widely in permeability to moisture and to oxygen (1, 4, 9) and in atmospheres of inert gases and atmospheres containing oxygen at various pressures (12). Antioxidants (11) and enzyme inhibitors (6) have been employed. Carbon monoxide will stabilize fresh meat color (2). Vacuum packaging has been favored by some (1, 4) and is said by others to be undesirable (2). The relation-

ship between film oxygen permeability and meat color is likewise in question, as is the related question of the effects of low vs. high oxygen tension on meat color.

No transparent film has been found which duplicates the color cycle that takes place in the small can, but several films closely approach the reactions in the can. They give a color history which almost makes centralized prepackaging feasible. Major attention is being given at this time to coated polyethylene and laminates of polyethylene.

Materials and Methods

The meat used in this investigation was choice beef loin. The cut samples used were approximately 0.5 inch thick and were 4 to 6 square inches in area. Redness of the top and bottom surfaces of samples before packaging was determined using the Hunter color and color difference meter. The value used to indicate redness was the a_L reading, using the L system on the meter. The standard used was a red enamel plate with values of L , 26.5; a_L , 26.6; and b_L , 12.7. Previously Rikert *et al.* (10-12) found that the a_L value was a direct indication of meat redness.

Samples were packaged in two different sizes of hermetic cans (307 × 113 and 211 × 011) and 14 types of plastic film materials as shown in Table I. Meat samples in cans were sealed under a vacuum of 29 inches using a Continental Can Co. can sealer No.

244-DS. Samples in film packages were sealed under a vacuum of 29+ inches using a Flex-Vac Model 6-9 sealer after a single preliminary gas flush with carbon dioxide. The head space in the 307 × 113 can was approximately 60%. The head space in the 211 × 011 can was approximately 10%.

All samples after packaging were stored in a Hill refrigerated showcase at a temperature of $38 \pm 2^\circ$ F. Samples were withdrawn from storage at regular intervals and the redness of their top and bottom surfaces was determined using the Hunter meter. Measurements were made immediately after removal from the package so that change in pigment state due to exposure to air would be minimized.

The findings as shown in Table I represent the results of 11 different test series which were carried out during a 1½-year period. Samples in cans were evaluated in all these series. Films which gave good color results were re-evaluated as a check on the first results. Duplicate or triplicate samples were taken at each storage period for each packaging material.

Irradiation. Samples in film packages of polyethylene coated with poly(vinyl alcohol) and in 211 × 011 cans were irradiated with beta rays at levels of 100,000 and 500,000 rep. using a 2-m.e.v. 500-watt Van de Graaff generator. Canned and film-packaged samples were irradiated in both the frozen and nonfrozen states. The nonfrozen samples were held under refrigeration

prior to irradiation. Comparable control samples (nonirradiated) were held in the same (frozen and nonfrozen) states during the period of irradiation. After irradiation, samples and controls were placed in the showcase at $38^\circ \pm 2^\circ$ F. and examined for color at regular intervals as previously described. Irradiation was accomplished on the day following packaging.

Aureomycin. Samples were immersed in an Aureomycin solution for 10 minutes and then were drained for 2 minutes or longer in a wire basket before being packaged in film packages of polyethylene coated with poly(vinyl alcohol). An 8- and a 15-p.p.m. solution of the antibiotic were employed. Nontreated controls were included in the tests.

Experimental Results and Discussion

Table I shows the average red color (a_L) of beef samples packaged in different films and in two sizes of cans at various intervals during a 14-day storage period. A week at 38° F. was regarded as the critical storage period for prepackaged meat. Seven days may be optimum for quality of the meat, but results were obtained for longer periods as it was desirable to know whether or not there was a likelihood of a change occurring on or about the seventh day. Therefore, results extending usually to the 14th day are shown. The average value shown for the storage period includes neither the initial (0-day) value nor the 13- to 14-day period value. An a_L value above 12 is

Table I. Redness of Beef at Various Storage Periods at $38 \pm 2^\circ$ F. in Different Packaging Materials
(a_L reading correlates directly with red color)

Side in Contact with Meat				No. of Samples Evaluated for Each Storage Period	Mean Redness (a_L Value) of Samples at Various Storage Periods										Av. for 7 Days Only
Outside		Inside			0 Days		2-3 Days		4-5 Days		6-7 Days		13-14 Days		
Film	Mil	Film	Mil		Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	
P	2	C	0.8	2	13.1 ^a		10.8 ^a		12.0 ^a		13.0 ^a		13.9 ^a	11.9	
	1		0.8	5	16.6 ^a		11.9 ^a		10.7 ^a		11.3 ^a		11.6 ^a	11.3	
	1.5		0.8	2	17.4 ^a		10.4 ^a		10.4 ^a		11.1 ^a		11.1 ^a	10.6	
C	0.8	P	2	2	18.2	15.7	6.8	7.0	9.5	9.0	10.3	9.0	8.5	9.6	8.6
	0.8		1	2	15.6	14.3	6.8	7.0	8.1	7.5	9.3	7.5	7.6	7.9	7.7
	0.8		1.5	4	18.2	16.6	6.1	7.3	6.9	6.9	8.8	7.8	7.7	8.5	7.3
PVC	2 (I) ^b	PVC		4	19.0	17.6	9.2	10.0	10.4	10.1	7.3	7.4	8.2	8.4	9.1
P	1.5	PVA	1	17	16.1	14.6	13.0	13.1	12.8	12.7	11.6	12.8	9.8	11.4	12.7
P	2	P	2	6	16.5	14.4	12.2	12.9	12.1	12.3	11.0	11.0	10.1	10.9	11.9
C	1.3														
PVC	2 (II) ^b	PVC		2	15.5	14.1	6.5	7.1	7.8	8.7	10.0	10.3	8.2	10.9	8.4
P	1.5	PVAc with sorbic acid	0.5	2	17.8	13.5	6.0	6.0	5.5	7.3	10.1	8.5	9.0	8.7	7.2
P	2	Mylar	0.5	7	14.7	13.4	11.0	11.8	11.4	12.0	11.1	11.1	7.2	7.4	11.4
PVAc	0.5	P	1.5	2	17.7	14.2	11.5	11.4	11.0	11.1	12.3	11.1	10.8	13.5	11.4
Plioform		C		7	15.4	15.3	11.4	11.8	10.6	9.4	11.3	8.3	8.7	9.9	10.5
Can 307 × 113 (60% head space)				8	15.8	14.8	6.8	11.3	8.7	12.4	11.1	12.5	11.7	13.0	10.5
Can 211 × 011 (10% head space)				15	16.8	15.1	13.7	14.0	13.5	13.9	13.6	13.0	13.2	13.8	13.9

P = Polyethylene

C = Cellophane

PVC = Poly(vinyl chloride) copolymer

PVA = Poly(vinyl alcohol)

PVAc = Poly(vinyl acetate)

^a Average of top and bottom a_L readings.

^b Two different films, not laminated but understood to differ in composition.

Table II. Redness of Beef Packaged in 211 × 011 Cans and in Polyethylene Coated with Poly(vinyl Alcohol) Film Packages after Irradiation with Beta Rays and Storage at 38 ± 2° F.

(a_L value correlates directly with red color)

Container	Treatment	Mean Redness (a_L Value) of Duplicate Samples at Various Storage Periods										
		0 Days		2-3 Days		4-5 Days		6-7 Days		13-14 Days ^a		Av. for 7 Days Only
		Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	
Irradiation Dose 100,000 Rep.												
Film package	NiNf	14.6	11.2	8.5	-9.4	9.6	11.6	10.3	11.9	7.5	11.6	10.2
	NiF	13.5	11.5	6.6	4.9	7.6	6.7	6.3	7.0	7.5	9.4	6.5
	INf	14.0	13.1	6.7	7.3	7.9	10.1	7.6	10.5	10.6	9.5	8.4
	IF	13.2	12.4	6.5	7.2	6.4	7.0	9.8	9.0	7.3	6.5	7.7
Can	NiNf	13.9	13.0	12.0	12.0	11.5	13.2	11.9	13.3	14.8	16.3	12.3
	NiF	15.3	13.4	12.2	12.7	11.4	13.6	13.5	13.0	16.1	13.6	12.7
	INf	15.9	15.2	14.0	15.2	14.5	14.1	13.1	13.1	16.7	15.2	14.0
	IF	13.9	12.7	13.5	13.6	13.1	13.8	13.1	13.1	14.6	14.3	13.7
Irradiation Dose 500,000 Rep.												
Film package	NiNf	17.0	16.3	12.0	14.0	13.4	16.5	12.0	12.0	12.9	12.9	13.6
	NiF	16.6	16.1	11.8	14.3	13.2	14.6	11.4	12.8	11.7	12.7	13.0
	INf	17.5	15.5	11.5	11.8	11.5	12.1	10.7	11.4	10.6	12.3	11.5
	IF	16.8	15.7	13.0	13.2	11.9	11.0	8.6	9.8	12.3	9.2	11.3
Can	NiNf	18.4	18.6	12.9	14.5	10.0	12.0	11.8	13.1	10.3	10.4	12.4
	NiF	18.3	16.2	14.6	15.3	12.8	13.2	10.6	11.0	11.6	13.7	12.9
	INf	18.1	16.8	10.0	10.5	10.6	10.8	11.6	9.7	9.0	9.8	10.5
	IF	16.8	15.8	9.5	14.7	11.4	14.0	10.4	13.6	11.8	13.2	12.3

Ni = nonirradiated
I = irradiated
Nf = nonfrozen
F = frozen

^a Storage period under irradiation dose 500,000 rep. is 20 to 21 days.

Table III. Redness of Beef Packaged in Polyethylene Coated with Poly(vinyl Alcohol) Film after Treatment with Aureomycin Solution

(a_L reading correlates directly with red color)

Meat Treated with	Mean Redness (a_L Value) of Duplicate Samples at Various Storage Periods										
	0 Days		2-3 Days		4-5 Days		6-7 Days		13-14 Days		Av. for 7 Days Only
	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	
Control, no treatment	17.8	15.2	9.5	10.3	9.9	10.9	8.5	11.0	9.4	11.1	10.0
Aureomycin hydrochloride 8 p.p.m.	17.7	13.9	8.5	9.3	8.0	7.4	8.0	10.2	10.4	9.5	8.9
15 p.p.m.	13.8	11.2	7.5	9.6	7.1	8.0	9.1	8.0	4.5	6.1	8.2

held to be acceptable red color, a value of 10-12 is questionable, and a value below 10 is not acceptable.

Nontreated Meat. Table I shows that the best red color of meat not treated with either irradiation or antibiotic was shown by the samples in the 211 × 011 cans which had only 10% head space. The samples in the 307 × 113 cans with 60% head space had poorer redness of top surfaces than of bottom surfaces during the first 4 or 5 days of storage. The top surfaces of samples packaged in cans with 10% head space had much better red color than the top surfaces of samples in cans with 60% head space during the first 5 days of storage. After 5 days, the difference was reduced although the former still had the better color rating.

Poorer red color of samples in cans with 60% head space is probably due to a large change of reduced myoglobin to metmyoglobin. The fact that this conversion is less in cans with 10% head space would indicate agreement with

findings of workers with myoglobin, itself, (3, 5) that conversion of reduced myoglobin to metmyoglobin is very low in the region of 1 mm. of partial pressure of oxygen. The amount of oxygen present in these 10% head space cans is very low due to their having about 5 cc. of absolute head space from which air is removed by vacuumizing, followed by a flush with carbon dioxide before final vacuum is drawn.

Samples in film-type package, which were poor in red color retention, reached a minimum in red color by the first, second, or fourth day of storage. After this period, they gradually increased in red color reaching a maximum return in redness by the seventh day of storage.

The film packaging material which gave the best results in terms of red color retention was polyethylene coated with poly(vinyl alcohol). Polyethylene-cellophane (polyethylene side in contact with meat), polyethylene-cellophane-polyethylene, polyethylene-poly(vinyl acetate)-polyethylene, and Mylar-poly-

ethylene (polyethylene in contact with meat) also showed good color.

When three different thicknesses of polyethylene laminated with cellophane were used with the polyethylene side in contact with the meat, the average red color values during the storage period were 11.9 for the laminate of 2.8 mils total thickness, 11.3 for the laminate of 1.8 mils total thickness, and 10.6 for the laminate of 2.3 mils total thickness.

When the same three thicknesses were used with the cellophane side in contact with the meat, the average red color values were 8.6, 7.7, and 7.3, respectively.

Irradiation. The average red color (a_L) of beef samples packaged in polyethylene coated with poly(vinyl alcohol) and in 211 × 011 cans and then irradiated at levels of 100,000 and 500,000 rep. is shown in Table II.

At 500,000 rep., meat samples irradiated in the film package were inferior in red color to nonirradiated controls for both the frozen and non-

frozen samples. Nonfrozen samples in cans, irradiated at this level, were inferior in red color to the nonfrozen controls. Samples in cans, irradiated in the frozen state at this level, appeared to be slightly inferior in red color to the frozen controls.

At 100,000 rep., meat samples irradiated in the can appeared to have slightly better redness than nonirradiated controls for both frozen and nonfrozen samples. Irradiated nonfrozen samples in film packages appeared to have slightly less redness than controls during storage, but irradiated frozen samples had slightly more redness than controls. Red color is preserved better when irradiation is done in the frozen state.

Aureomycin. The data shown in Table III indicate that a dip into a water solution of aureomycin hydrochloride of either 8- or 15-p.p.m. concentration before packaging serves to decrease somewhat the redness of beef samples during storage. This may be due to the fact that certain genera of bacteria such as *Achromobacter* help maintain or return the red color of meat

during storage (7). A wide-band antibiotic such as aureomycin inhibits bacteria.

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Literature Cited

- (1) Ball, C. O., Clauss, W. E., Stier, E. F., *Food Technol.* **11**, 277 (1957).
- (2) Bratzler, L. J., Proc. Seventh Research Conf., Council on Research, American Meat Institute, March 24-25, 1955.

- (3) Brooks, J., *Biochem. J.* **23**, 1391 (1929).
- (4) Clauss, W. E., Ball, C. O., Stier, E. F., *Food Technol.* **11**, 363 (1957).
- (5) George, P., Stratmann, C. J., *Biochem. J.* **51**, 103 (1952).
- (6) Grant, N. H., *Food Research* **20**, 250 (1955).
- (7) Halleck, F. E., Ph.D. thesis, Rutgers University, New Brunswick, N. J., 1952.
- (8) Landrock, A. H., Wallace, G. A., *Food Technol.* **9**, 194 (1955).
- (9) Pirko, P. C., M.S. thesis, Iowa State College, Ames, Iowa, 1956.
- (10) Rikert, John A., Ball, C. Olin, Stier, Elizabeth F., *Food Technol.* **11**, 520 (1957).
- (11) Rikert, John A., Bressler, Lawrence, Ball, C. Olin, Stier, Elizabeth F., *Food Technol.* **11**, 567 (1957).
- (12) *Ibid.*, p. 625.

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FOOD ADDITIVE ANALYSIS

Composition of Polyoxyethylene (8) Stearate

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The composition of polyoxyethylene (8) stearate was investigated to determine its safety as a food additive. This compound—made by reacting 7.4 moles of ethylene oxide per mole of commercial stearic acid—contains unesterified polyoxyethylene glycol and polyoxyethylene glycol monostearate, distearate in the molar proportions of 1.1 to 2.0 to 1.0, with free and esterified polyethylene glycols having equal polymer lengths. After allowance for small amounts of catalyst and water, the results are those expected if rapid ester interchange occurs. The polyglycols through the nonamer comprise 81% of the total polyglycols and the polymer distribution approximates a Poisson distribution.

POLYOXYETHYLENE (8) STEARATE (Myrj 45, Atlas Powder Co.) is made by reacting ethylene oxide with commercial stearic acid. The molar proportion of ethylene oxide to stearic acid is 8 to 1 if the stearic acid is assumed to be pure—i.e., to have a molecular weight of 284. As commercial stearic acid contains substantial proportions of fatty acids of lower molecular weight, such as palmitic and oleic, the acids used for the production of Myrj 45 have an average molecular weight of 270. In the manufacture of Myrj 45, 1.235 parts by weight of ethylene oxide react with one part of

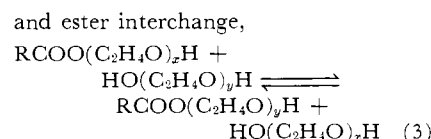
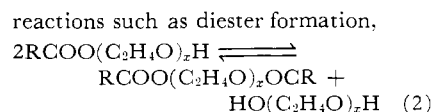
stearic acid, using 0.3% sodium methylate as catalyst. After reaction, the product is deodorized by heating under vacuum, bleached with hydrogen peroxide, filtered, and adjusted to 2.5 to 3.0% water.

The general over-all reaction is:

$$\text{RCOOH} + x\text{C}_2\text{H}_4\text{O} \longrightarrow \text{RCOO}(\text{C}_2\text{H}_4\text{O})_x\text{H} \quad (1)$$

The final product contains polyoxyethylene chains of varying lengths with x averaging 7.4.

According to other investigators (11, 13), conditions are favorable to other



Myrj 45 is therefore expected to be a mixture of polyoxyethylene glycol monostearate, polyoxyethylene glycol distearate, and unesterified or "free" polyoxyethylene glycol. If Reactions 2 and 3