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USE OF ETHYLENE ABSORBERS IN EXTENDING PRODUCE SHELF LIFE

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1. INTRODUCTION

Supplying military personnel with high quality fresh fruit and vegetables (FF&V) outside the continental United States has always been a major challenge. Each location has its own unique problems. Most of the FF&V consumed by the troops in the Pacific and Far East come from a long supply line over the ocean from the West Coast. Although ships in the Mediterranean Sea are supplied with produce from local countries, they only take on board that amount which can be consumed before spoilage occurs and, therefore, require frequent resupply.

Ethylene-Accelerated Spoilage

Ethylene, as a natural plant hormone produced by metabolism in most fruits, initiates and accelerates the ripening of fruit and causes vegetables to deteriorate. This unavoidable process is a major problem, since in almost all applications noncompatible fruits and vegetables (i.e., ethylene emitters and ethylene-sensitive items) are stored and/or shipped in the same container. If the level of ethylene could be kept as low as possible, it would be possible to slow the maturation of the fruits, protect the vegetables, and reduce spoilage to a minimum.

Accordingly, one of the simplest ways was used to remove ethylene from the atmosphere that involves absorption and then oxidation to produce CO_2 and H_2O upon reaction with potassium permanaganate. Several commercial companies produce pelletized forms of alumina coated with potassium permanganate. These were obtained and evaluated.

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2. MATERIALS AND METHODS

Absorbing Blankets

The blankets were obtained on the commercial market. They were analyzed chemically and physically by standard methods, except for potassium permanganate ($KMnO_4$). This analysis was done by a spectrophotometric procedure in which the beads are crushed and the $KMnO_4$ dissolved in water. The absorption at 525 nm was then compared to a calibration curve developed for determination of weight percentage.

The atmosphere inside refrigerated rooms was analyzed for ethylene by drawing air samples into vacuum canisters and then injecting a small aliquot into a gas chromatograph. This was done on a Perkin-Elmer Gas Chromatograph, Model Sigma 3b equipped with a flame ionization detector. A stainless steel tube, five (5) feet long and 1/8 inch O.D. packed with Carbosieve S II 60-80 mesh was the chromatograph column used. The flow rate of Helium, the carrier gas, was 30 ml per minute. Hydrogen was the fuel and compressed air supplied the oxygen for the ionization detector flame. Oven temperature was maintained at 200 degrees centigrade. Injector and detector temperatures were set at 225 and 275 degrees centigrade, respectively. Peak heights and retention times for the standards and samples were measured by a linear strip chart recorded Model 385 and a Hewlett-Packard reporting intergrator Model 3390A. The concentration of ethlyene in the samples was determined by an external standard calibration method. Using a sample size of 0.5 ml, the lower detection limit was 0.2 parts per million.

Fresh Fruits and Vegetables-

The experimental produce was obtained through normal Government procurement channels for each of the experiments. Inspection of the produce was done by the US Army and the Defense Personnel Support Center (DPSC) inspectors according to USDA procedures.

3. RESULTS AND DISCUSSIONS

LABORATORY STUDIES

Absorber Characteristics: Chemical-Physical

A chemical analysis of the material was done specifically to determine the amount of potassium permanganate in each commercial product. The percentages ranged from 2.6 to 5.0%. Analyses were also made of the porosity, surface area, and particle size distribution of the pellets. These were made in order to relate these characteristics to possible differences in absorptive capacity of each absorber. Values in Table I show there is a wide range of porosities, pore volume, density, etc., in the commercial products tested.

TABLE I

Physical Characteristics of Various Commercial Ethylene Absorbers

Sample	Bead Density g/cc	True [a] Density g/cc	%Porosity[a]	Median Pore Size-um	Pore Size Range-um
Purafil	1.29	3.15	59.1	1.8	0.5-4.0
Air Repair	1.42	2.08	31.7	0.9	0.5-1.5
Ethysorb	1.61	2.04	21.1	2.0	0.8-3.0
Carusorb	1.62	2.23	27.4	2.0	1.0-3.0

[a]-Pycnometry

The color of the potassium permanganate/alumina pellets is distinctive. Before use, they are bright purple; during use, they change color and become completely brown indicating that they are totally expended. Consequently, the user can easily determine with a color chart when the capacity for absorption is depleted and the material needs to be replaced.

Two features are important in characterizing the functional capability of the absorbing material. The first is its ability to quickly reduce the level of ethylene in a refrigerated storage chamber to an acceptable level. The second is its ability to sustain a low level for an extended period. Fig. 1 shows that with a background level of 60 ppm ethylene without absorbent, three of the four samples tested were able to reduce the level below 1 ppm after one day. It shows also that the time over which the absorber maintains this level is closely correlated to the percent permanganate in the fresh sample. These tests were made through a contractual arrangement with Mine Safety Appliances (MSA).

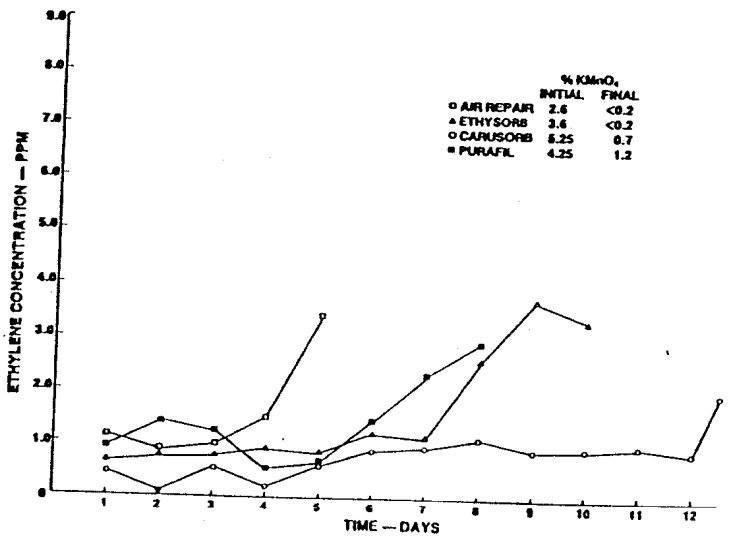

FIG. 1 CAPACITY OF COMMERCIAL ETHYLENE ABSORBERS

The effect of exposing various types of absorbers to ethylene was also measured using apples as a source of the gas. Measured amounts of three different absorbers were placed in a circulating air system inside a 550 cubic foot refrigerator containing 500 pounds of apples. The percent permanganate remaining was measured versus time as shown in Fig. 2. It appeared that most of the permanganate was inaccessible in the Carusorb sample. Also, Purafil reacted quicker and more completely, suggesting that higher porosity and higher pore volume makes $KMnO_4$ more accessible.

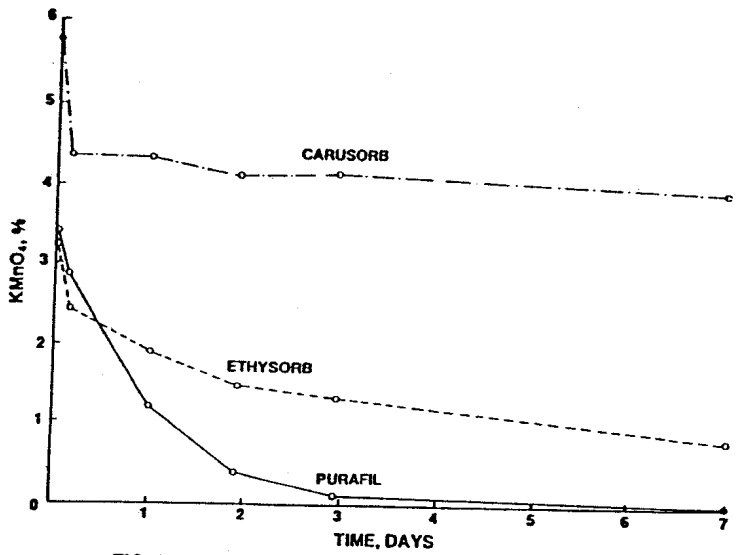

FIG. 2 EFFECT OF ETHYLENE ON % $KMnO_4$ FOR VARIOUS COMMERCIAL ABSORBERS

Testing Absorbers with FF&V

Several tests were made with the various types of commercially available absorbers using selected FF&V stored at 40°F in a 500 cubic foot refrigerated chamber. Good results were obtained by comparing spoilage with and without the absorbers, again using apples as the source of ethylene. In all tests involving absorbers, the air was passed over fixed amounts of pellets; whereas in control tests without absorbers, a small environmental chamber was used, the proportion of apples to volume being essentally the same. The results show that the shelf life of plums, apples and avocados was definitely longer when absorbers were present.

FIELD VALIDATION

Supply Chain Considerations

Before undertaking the field tests, a survey was conducted of the FF&V supply chain to overseas bases. In Europe, the use of absorbers would be appropriate in storage chambers on user ships at sea as well as on the supply ships. There would also be an impact on submarines, which are at sea for extended periods without contact or resupply. In the Pacific Area, including the Far East, most of the FF&V used by military personnel is sent by surface ships from the West Coast.

Mixed, noncompatible fruits and vegetables are loaded into sea containers; these are sealed and maintained at refrigerated temperatures for voyages that can take three to four weeks. Reports from those responsible for the logistical support indicate that spoilage ranges as high as 30% or more for individual produce. There is also a large amount of ethylene-sensitive produce being air-lifted, at high cost, to many locations in the Pacific.

Test Approach

The basic approach to the field-testing of the ethylene absorbers was to compare mixed, noncompatible produce stored at controlled temperatures with and without ethylene absorbers, simultaneously if possible. Among the variables to be monitored were the levels of ethylene present and the rate of spoilage.

Field Test I: Supply Ship in Mediterranean

The first, full-fledged field test took place in the Mediterranean aboard a supply ship. It was done in two consecutive, two-month periods in one storage hold, first with and then without ethylene absorber blankets. Test samples of mixed fruits and vegetables were picked up in Spain and stored in the refrigerated hold along with the ship's normal supply. During this two month period, the ship picked up and then delivered produce to other ships at sea about every two weeks, so that the total ship's supply and the consequent ethylene level varied. Seven fresh Ethysorb blankets were hung each month in front of the refrigerated air intake. For the second two month period, the ship picked up similar produce from Italy and stored it <u>without</u> using absorber blankets.

Inspection of the normal supply of the produce was done by the ship's personnel. Gas samples of the atmosphere in the refrigerated hold were also taken with vacuum bottles and returned for analysis. Shelf life of the protected FF&V was extended well beyond that of FF&V not protected by absorber blankets. Fig. 3 indicates that the point of 30% spoilage for apples is nearly twice as long for absorber protected than unprotected fruit. The U.S. Army inspectors and ship's personnel commented favorably on the quality of the produce that had been stored for several weeks.

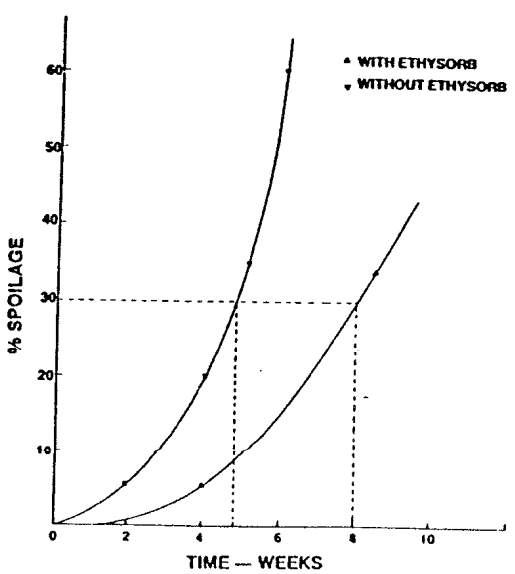

FIG. 3 EFFECT OF ETHYLENE REMOVAL ON SPOILAGE RATE OF APPLES — ABOARD SHIP

Field Test II:Container Ships to Korea

This test was the most controlled of all the field tests to date. In cooperation with logistic personnel in Alameda, CA, a three week shipping test to South Korea was arranged. Large lots of FF&V were split and placed into two identical 40 ft sea vans, one with and the other without absorber blankets placed near the air inlet to the cooling system operating at 36°F. The produce was inspected before loading in Alameda and after unloading from the container ship in Pusan, South Korea. The atmosphere in each van was also sampled for the concentration of ethylene.

Upon arrival in Pusan, the atmosphere in the test van with the absorber blankets had an ethylene concentration of 1.8 ppm, while the atmosphere in the control van had 29.2 ppm. The blankets had an average about 25% of the available potassium permanganate remaining. They were in need of replacement, since their efficiencies were at a low level.

TABLE II

South Korea Inspection Results - Field Test II

Product	Test Van	Control Van
Cabbage	Fresh, Crisp, Good Green Color	Yellowish Green 11% Decay
Celery	Fresh, Crisp 3% Decay-Tops	100% Rot Surveyed
Peas	Fresh, Green <1% Rot	Fresh, Green 14% Rot, Mold
Escarole	Some Decay At Tips	100% Decay Surveyed
Pears	Mostly Firm	Firm To Ripe Many Ripe
Nectarines	Mostly Hard	Mostly Hard To Firm, 13% Decay
Kiwi Fruit	Mostly Firm 1% Decay	Mostly Ripe 2% Decay

Table II summarizes the effect of ethylene removal on produce quality. The fruits and vegetables in the absorber-protected ISO container were in excellent condition. The vegetables had minimum decay and spoilage, and the fruits were firmer and less ripe. In the control ISO container, many of the green leaf vegetables were completely spoiled, and most of the fruits were ripe enough for immediate use.

Field Test III: Normally Air-Shipped Items Sent by Surface Vessel to South Korea.

Because of the concern about the high cost of air-shipping increasingly larger amounts of "sensitive" fresh fruits and vegetables overseas, another cooperative sea van test to South Korea was conducted. It was intended to determine if some or all of those

items normally air-shipped could be safely sent by surface vessel using absorber blankets. Two vans again were set up in a manner similar to Field Test II, except that items normally air-shipped were included on each van and that the overload trucking of the FF&V from Pusan to Yongsan was included. Produce was again inspected in Alameda and at several stops in South Korea until the final destination in Yongsan. Most importantly, a compromise temperature of 40°F was selected this time, since both 34°F and 50°F items were included.

The results show that many air-lifted items, such as avocados, limes, celery, corn, and tomatoes, could be converted to surface shipment. Other items such as grapes, melons, peaches, plums and nectarines could be converted to surface shipment when they are in season in the U.S. Some items such as strawberries, asparagus, sweet peppers, mushrooms, etc. should still be air-shipped. There was excessive deterioration of the green leaf vegetables indicating that when temperature incompatible produce are mixed the lower temperature should be selected especially with large amounts of green are present.

COMPARATIVE ECONOMIC ASPECTS

Since it is essential that the efficiency of the absorbers be normalized for cost, the MSA Research Corporation conducted a economic and technical comparison of commercially available ethylene absorbing systems. MSA not only considered potassium permanganate absorbers, but also evaluated other absorbing materials, catalytic oxidizers, and even ventilation of the refrigerated storage area as ways of removing ethylene.

The MSA results show that the lowest cost method for keeping the level of ethylene low in the refrigerated storage areas involves the use of potassium permanganate absorbers, followed next by ventilation and finally by catalytic oxidation. With respect to the permanganate absorbers, although the rate of reducing the ethylene in a storage area to an acceptable level may vary slightly among brands because of differences in surface area or porosity of the pellets, each brand performed satisfactorily. The total capacity, i.e., the ability of the absorbing material to maintain a low level of ethylene, is in most cases proportional to its weight percentage of potassium permanganate.

In order to know the overall economic benefits of using ethylene absorbers, it is necessary to determine the savings due to reduced spoilage in a shipment and to compare it to the cost of absorbers required. Using the example of the shipment to South Korea, the estimated savings due to a reduction in spoilage at the destination was $928, while the cost of the absorbers was $160, giving a net benefit of $768. This benefit does not take in account the <u>indirect loss</u> of shipping bad produce, post-shipping loss due to shorter remaining shelf life, or the lowered morale due to nonavailability of the fresh produce (see Table III).

Table III

Economic Analysis Of Absorber Usage For Field Test II To South Korea

	Weight-lbs.	Cost-$
Test Van		
Produce	16,070	6,550
Produce Spoilage	0	0
Four Absorber Blankets		160
Control Van		
Produce	16,070	6,550
Produce Spoilage - 100% Surveyed	2,025	688
Partial Spoilage	620	240
Total Produce Lost	2,645	928

NOTE: Further spoilage before consumption of products is retarded because vegetables have more remaining shelf life and fruits arrive less mature and ripe.

4. CONCLUSION

It is clear from these studies that ethylene absorbing blankets containing alumina coated with potassium permanganate should be used in all fruit and vegetable storage areas in order to ensure maximum shelf life at an affordable cost.

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