USE OF ETHYLENE ABSORBERS IN EXTENDING SHELF LIFE

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List of Figures:

Fig. 1 – IN-HOUSE TESTING OF ABSORBERS

List of Tables:

Table II - SOUTH KOREA INSPECTION RESULTS - FIELD TEST II

INTRODUCTION

Background

Supplying the military 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. The majority of the FF&V consumed by the troops in the Pacific and Far East come from a long, sometimes more than three week, 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.

Nature of the Problem

Ethylene is a natural plant hormone produced by metabolism in most fruit. It 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 we could keep the level of ethylene as low as possible, we would be able to slow the maturation of the fruits, protect the vegetables, and reduce spoilage to a minimum.

Technical Strategy

One of the simplest ways to remove ethylene from the atmosphere is to absorb and oxidize it with potassium permanganate to produce CO₂ and H₂O. Several commercial companies produce pelletized forms of alumina or zeolite coated with potassium permanganate. These were obtained and evaluated according to the following plan:

- Test/Characterize Absorbing Material
- Test Absorbers on IN-House FF&V
- Field-Test Absorbers in Troublesome Supply Locations
- Compare Economic Aspects

RESULTS AND DISCUSSION

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 2.5 to 5.0. We also did analysis of the porosity, surface area, and particle size distribution of the pellets. These were done in order to be able to relate these values to possible differences in absorption capacity of each absorber.

The color of potassium permanganate 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.

The absorptive capacity and efficiency of each type of absorbent material were evaluated in the chemical laboratory by subjecting a measured amount of pellets over a period of time to a known concentration of ethylene from a compressed gas bottle. Two measurements were made: the rate of depletion and the time to total completion. The first reflects the ability of the absorber to quickly reduce the level of ethylene to an acceptable level and the second, its ability to sustain this low level for an extended period. These tests were also made by Mine Safety Appliances as part of a contract to do the "Comparative Economic Evaluation of Commercially Available Ethylene Removal Systems."

Testing Absorbers In-House with FF&V

Several in-house tests were made with the various types of commercially available absorbers using selected FF&V stored at 40°F. Good results were

obtained by comparing spoilage with and without the absorbers, using apples as the source of ethylene. In all cases, one storage facility was used in which the air was passed over fixed amounts of pellets, while a small environmental chamber was used without absorbers as a control. These results show that the shelf life of plums (see Fig. 1), iceberg lettuce, and tomatoes were definitely longer when absorbers were present.

Field-Testing in Troublesome Supply Locations

Supply Chain Considerations. Before undertaking field tests, a survey was conducted of the FF&V supply chain to overseas bases. In Europe, the US forces buy their FF&V from the local market. Ships in the European and Mediterranean waters are also supplied from local markets in countries that have agriculture methods similar to ours. Supply ships load up at port and deliver the FF&V to combat ships at sea. Ethylene absorbers would have their greatest impact in storage containers on the user ships at sea as well as on the supply ships. There would also be an impact on submarines, which sometimes are at sea for months without contact or resupply. In the Pacific Area, including the Far East, the large majority of the FF&V used by US forces is sent by surface ship 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 Defense Supply Region – Pacific (DSR-PAC) indicated that spoilage ranged as high as 30% or more for individual produce. There was also a large amount of ethylene-sensitive produce being air-lifted, at high cost, to many locations in the Pacific.

<u>Test Approach.</u> The basic approach to the field-testing of the ethylene absorbers was to compare mixed, non-compatible 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 (USS Sylvania). Our first, full fledged field test took place in the Mediterranean aboard the supply ship USS Sylvania. It was done in two consecutive, two-month periods in one storage hold, first with and then without ethylene absorber filters. 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 the two-month period, the Sylvania picked up and delivered produce to the 6th Fleet at sea about every two weeks, so the total ship's supply and the consequent ethylene level varied. For the second two-month period, the ship picked up similar produce from Italy and stored it without absorber filters. Shelf life of the protected FF&V was extended well beyond that not protected by absorber filters. The army inspectors and ship's personnel were impressed by the quality of the produce after being stored for several weeks.

<u>Field Test II (Korea by Surface Vessel).</u> This test was the most controlled of all the field tests to date. In cooperation with DSR-PAC in Alameda, CA, we set up a three-week shipping test to South Korea. Large lots of FF&V were split and placed into two identical 40 ft. sea vans, one with and one without absorber filters placed near the air inlet to the cooling system operation at 36°F. The produce was inspected by a Quality Assurance Specialist from DSR-PAC and a Natick Project Officer 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 filters had an ethylene concentration of 1.8 ppm, while the atmosphere in the control van had 29 ppm. The filters had an average of 25% of the available potassium permanganate remaining. They were ready for replacement, since their efficiencies were at a low level.

The fruits and vegetables in the absorber-protected van were in excellent condition. The vegetables had minimum decay and spoilage, and the fruits were firmer and less ripe. In the control van, many of the green leaf vegetables were completely spoiled and most of the fruits were ripe enough for immediate use.

Field Test III (Korea by Surface Vessel of Normally Air-Shipped Items). Because the Commander of the Troop Support Agency (TSA) in Ft. Lee, VA was very concerned about the high cost of air-shipping increasingly larger amounts of "sensitive" fresh fruits and vegetables overseas, another cooperative DSR-PAC/Natick 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 filters. 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 overland trucking of the FF&V from Pusan to Seoul was included. Produce was again inspected in Alameda and at several stops in South Korea until the final destination in Seoul. 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.

Comparative Economic Aspects

Since it is essential that the efficiency of the absorbers be normalized for cost, the MSA Research Corporation conducted a wide ranging economic and technical comparison of all commercially available ethylene absorbing systems.

It looked not only at potassium permanganate absorbers, but it also evaluated other absorbing material, catalytic oxidizers, and even ventilation of the refrigerated storage area as a means of removing ethylene.

The MSA results showed 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 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 percentage of potassium permanganate.

In order to know the overall economic benefits of using ethylene absorbers, you have moreover, to determine the savings due to reduced spoilage in a shipment and 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 destination was \$928 while the cost of the absorbers was \$160, thus a net benefit of \$768. This benefit does not take into account the indirect loss of shipping bad produce, post shipping loss due to shorter shelf life remaining, or the lowered morale due to non-availability of the fresh produce.

Purchase Description

As with most of Natick's developmental efforts, the culmination of this work is a purchase description that will allow the government to procure effectively and economically the items needed by the military.

All of the necessary information has been gathered and compiled, and we are in the process of developing a Commercial Item Description, or CID, which allows the Service to buy adequate items off the commercial market with a minimum amount of product specifications and quality assurance provisions. This purchasing instrument requires the manufacturer to certify that the item is sold commercially and meets the salient characteristics specified as well as his own specifications and standards. The government still retains the right to test and verify compliance. Though it will be several months before the CID will be complete and in the system, local purchases can be and are being made based on our technical description.

CONCLUSION

It is clear from these studies that ethylene absorber filters containing zeolite 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. Many ships and commands in the Navy are successfully using the filters.

When the CID is in the system, the cost of the filters will be reduced due to centralized purchasing.

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FIG. 1 – IN HOUSE TESTING OF ABSORBERS

*ABSORBERS

*CONDITIONS - 40°f FOR 10 WEEKS *PRODUCE - PLUMS WITH APPLES

*RESULTS - TEST CHAMBER
- CONTROL CHAMBER

TABLE II – SOUTH KOREA RESULTS – FIELD TEST II

44% SPOILED

100% SPOILED

<u>PRODUCT</u>	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

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