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Past studies in the Western Regional Research Laboratory on cut dried fruits have been concerned with collecting data on the effects of time and temperature, moisture and sulfur dioxide content on product stability — a much needed basis for establishing conditions for optimum storage stability. The data on sulfur dioxide content has been used by the Dried Fruit Association of California and representatives of the United States Foreign Agricultural Service in negotiations with foreign countries for liberalizing restrictions imposed on the use of sulfur dioxide in dried fruits. At the present time most of the European countries permit 2,000 parts per million of sulfur dioxide in cut dried fruits and we have heard recently that Japan has now followed suit. Much as we would like to, and other countries would like us to, we cannot dispense with this effective preservative.

We might on first glance consider that 2,000 parts per million of sulfur dioxide is quite a generous allowance. However, in actual fact, this restriction severely limits the shelf-life of the products once they have entered a country. As soon as sulfur dioxide is applied to fruit, it begins to break down, to disappear. When the level drops to one third of its original value, about 700 parts per million as-is basis, there is no longer sufficient sulfur dioxide to protect the fruit, and spoilage and darkening become noticeable. The fruit is then unsalable.

Temperature of storage has a profound effect on the rate of sulfur dioxide loss as we can see from an examination of the curves in Figure 1. At 90° F. storage, the shelf-life estimated for sulfur dioxide levels starting at 2,000 parts per million and falling to 700, is approximately one and one-half months; at 70° F., five to six months. Any high temperature abuse, no matter how short, is "remembered", so to speak, by the product. That is to say, the effect of storage temperature abuses are cumulative. It would be highly desirable, therefore,

to be able to stabilize the sulfur dioxide against this decay.

In order to extend shelf-life of cut dried fruits and still stay within these arbitrarily imposed limits it is necessary to reduce this rate of sulfur dioxide loss, but to do this we first must determine the manner in which sulfur dioxide is destroyed and then what factors accelerate this destruction. Careful studies at this laboratory have conclusively shown that, within the limits of our methods of analysis, all the sulfur dioxide lost appears as sulfate ions:

$$SO_2 + 1/2O_2 = SO_3$$
 and $SO_3 + H_2O = H_2SO_4$.

Now, it is well known that such an autoxidative conversion is accelerated by exposure to air, moisture, radiation (sunlight), heat, and metals such as iron, manganese, nickel, etc. Of these factors, exposure to light, air and metals were considered controllable.

The effect of sunlight is evident in data in Figure 2 in which peaches dried in a tunnel dryer are compared with peaches dried in the sun. The effect of exposure to light in storage is only of concern, however, with dried apples. Data for sulfur dioxide loss and sulfate formation in dried apples stored in the dark and exposed to fluorescent lighting is plotted in Figure 3. It is quite evident that exposure to light accelerated the rate of conversion to sulfate. In Figure 4, on the other hand, it is seen that the stability of sulfur dioxide in dried peaches is not particularly changed by exposure to light. This is also true for apricots, although, there is a slightly observable difference.

Exposure to the oxygen of the air can be controlled by hermetically sealing the dried fruit in cans or vacuum sealing in impervious films such as "Saran". The air in bags and containers may be replaced by flushing with inert gases such as nitrogen or products of natural gas combustion. These measures are rather expensive and involve treatments on each individual retail package. Another solution to the problem is to remove the oxygen from the container with an oxygen scavenger system. The scavenger and retail packets (slowly permeable to air) are sealed in an impermeable (Saran) bag inside the shipping carton. When the carton

is opened for display in the retail store, the impermeable (Saran) bag and scavenger are thrown away. The contents of the scavenger are non-poisonous, though they would not improve the fruit, if they were mixed with it.

In Figure 5 there is given the composition of the scavenger mixture and curves showing the rate of oxygen uptake. The active ingredient is sodium bisulfite which like sulfur dioxide in the dried fruit is oxidized by the oxygen in air to sulfate. The carbon, ferric chloride and hydrogen peroxide simply serve to accelerate the reaction. In order to push the reaction rapidly to completion, an 80% excess of sulfite is used. At room temperature practically all of the oxygen in a one liter container is removed in a half day.

In Figure 6 we see apricots on the left stored 80 days at 90° F. without oxygen scavenger and on the right 80 days with scavenger. It is hoped that in the printed reproduction the clearly darker appearance of the apricots not stored with scavenger is visible. The actual sulfur dioxide retention data for the two storage samples appear in Figure 7. The fruit in the bags stored with the scavenger lost only 570 parts per million of the sulfur dioxide whereas the controls stored without oxygen scavenger lost 1600 parts per million, almost three times as much! In the bottom line is given the data for alcohol extractable color, which also illustrates the improvement (lightness in color) gained by oxygen removal. It must be kept in mind that under this proposed handling procedure, atmospheric control would be effected only during warehousing and transportation and as long as the package remained intact and the capacity of the scavenger was not exceeded.

Control of trace metal activation of the conversion of sulfur dioxide to sulfate is best achieved by using sequestering agents, since in processing and fruit handling, metal contamination cannot be avoided. A series of these sequestering agents appears in Table 1 in which they are listed from left to right in increasing order of avidity for iron.

Unfortunately, the edible compounds maltol and kojic acid form bright red adducts with iron.

Ethylenediamine tetraacetic acid (EDTA), however, is permitted in foods and is quite effective

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as seen in Figure 8 in which is shown an apple slice treated with a 1% solution of EDTA and another, untreated, both stored at 90° F. for 17 days. We have no data on sulfur dioxide retention for this experiment but the benefit is visibly evident.

To summarize -- an extension of shelf-life for cut dried fruit (possibly a doubling) can be realized by controlling agents known to accelerate the conversion of sulfur dioxide to sulfate. Separately, or in combination, use may be made of an oxygen scavenger for removing oxygen, controlling exposure to light during drying and in storage, and, finally, reducing the metal activation by applying ethylenediamine tetraacetic acid or other permitted sequestering agents.

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(June 24, 1963)

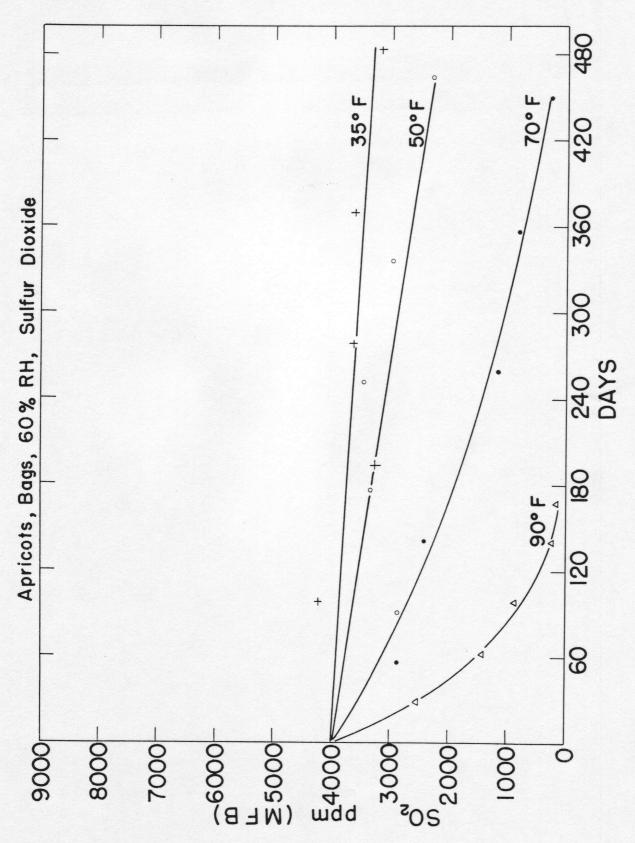


Fig. 1 Effect of temperature during storage on sulfur dioxide loss in dried apricots.

EFFECT OF DRYING METHOD ON SULFATE FORMATION IN SULFITED FRUITS

		On moisture	On moisture-free basis
Drying method		202	S04
		mdd	ppm
Sun drying	Apricots	3570	3360
Sun drying	Peaches	2750	2940
Dehydration	Apples	3360	029

Fig. 2 Sulfate formation in sun-dried and commercially dehydrated cut fruits.

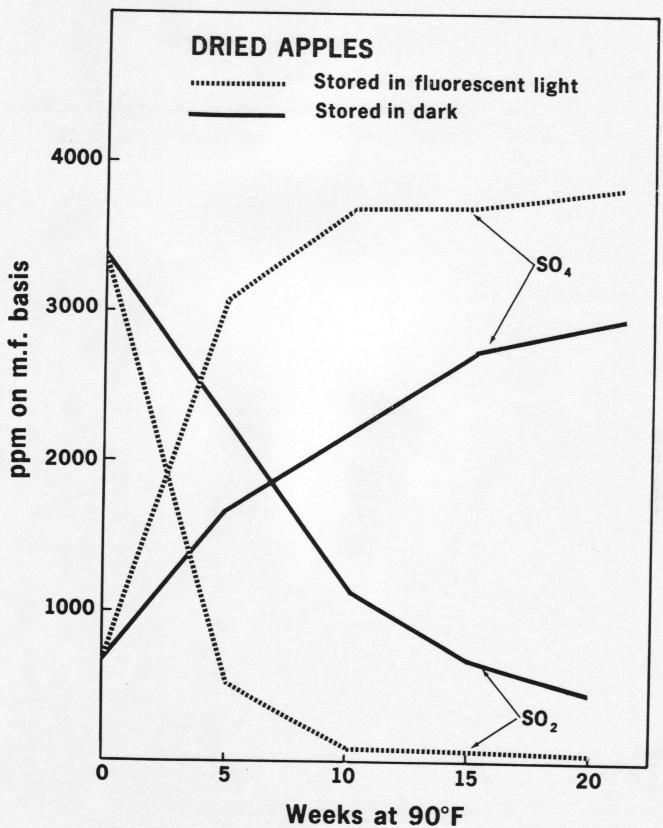


Fig. 3 Sulfite loss and sulfate formation in dried apples stored in the dark and exposed to fluorescent lighting.

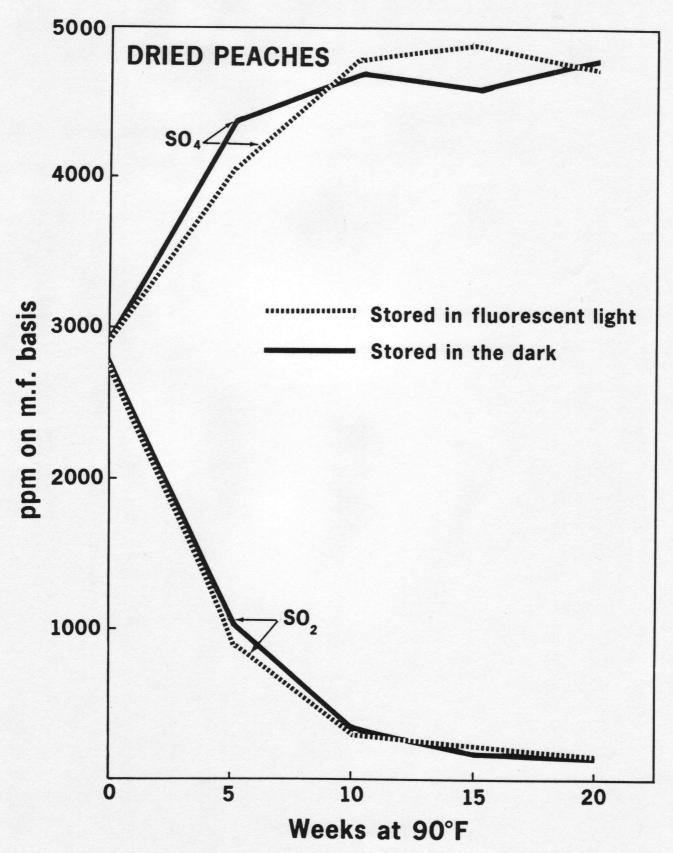


Fig. 4 Sulfite loss and sulfate formation in dried peaches stored in the dark and exposed to fluorescent lighting.

RATE OF OXYGEN SCAVENGING

3.6g NaHSO₃ per liter of air (Excess: 1.8 × theoretical amount)

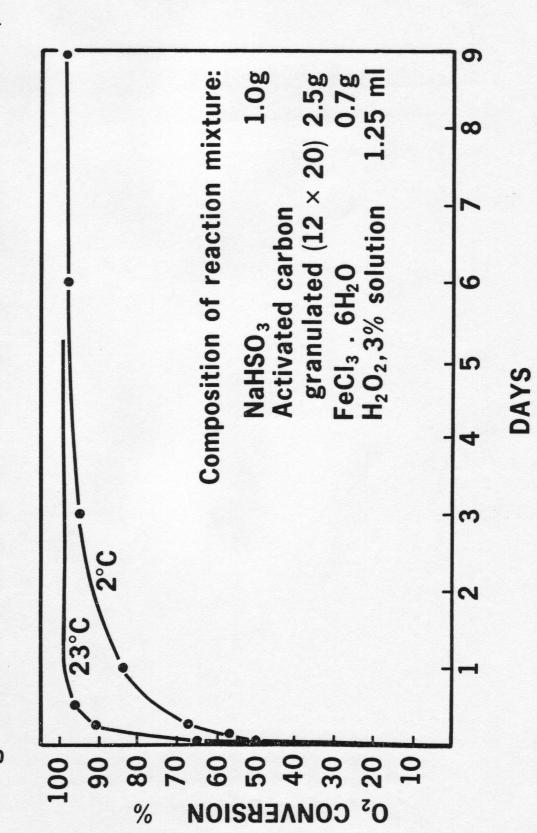


Fig. 5 Oxygen scavenger composition and rate of oxygen uptake.



Apricots stored at 90° F. for 80 days. A. Control stored in sealed outer saran bag without oxygen scavenger.

B. Sealed in outer saran bag containing oxygen scavenger

Fig. 6

packet.

Dried apricots packed commercially in cellophane bags stored 80 days at 90°F.

B	Before storage	Stored with 0 ₂ scavenger in ambient air	Stored without 0 ₂ scavenger
Moisture, %	23.6	23.0	22.8
$S0_2$, ppm.	2820	2250	1220
Color (0.D., 50% alc. ext.)	0.100	0.245	0.390

Fig. 7 Effect of oxygen scavenger on sulfur dioxide loss and 50% alcohol extractable color (browning) in dried apricots.

STABILITY OF Fe COMPLEX IN INCREASING ORDER:

Citric acid

Tartaric acid

Polyphenol (Quercetin)

Polyphosphate

Pyrone (Maltol Kojic acid)

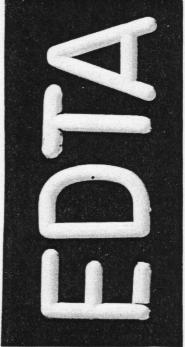
Malic acid

Cysteine

EDTA

Iron binding power of a series of classes of chelating agents. (EDTA is ethylene diamine tetraacetic acid). ω Fig.







Effect of dip in 1% solution of ethylene diamine tetraacetic acid (EDTA) on darkening of apple slices stored at 90° F. for 17 days. Untreated control is on the left.

Fig. 9