INJURY TO PEARS CAUSED BY PAPER LINERS IMPREGNATED WITH SODIUM SILICATE[1]

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INTRODUCTION

Pears of all varieties have one or more layers of stone cells just under the skin, and because of the mechanical resistance offered by these cells the pears are very susceptible to damage by rubbing or bruising. Moreover, the skin of pears usually turns dark brown or black after an injury; hence, after the treatment ordinarily given to pears during the picking and packing processes they are likely to show some discoloration when they reach the market. For the last several years, however, a brown spotting has been observed on certain varieties of pears, both in carload shipments just arrived on the market and in cold-storage lots, which is different in some respects from that caused by rubbing or bruising. It is found on fruits that have been in contact with the corrugated paper used for lining the boxes, or with the excelsior-filled pads used in pear boxes to prevent bruising of the fruit. The spotting is brown in color and usually only superficial. In many instances, especially with the Bosc pear, it occurs in bands crosswise of the fruit, corresponding to the corrugations of the paper liner (fig. 1, A). Often, however, it occurs only as an irregular-shaped brown spot one fourth to 1 inch in diameter. The spotting is sometimes found on all the fruits in a box that touch the corrugated paper and may thus involve one third or more of the contents of a box. It has not been seen on pears or the portions of pears that have not been in contact with a corrugated liner or an excelsior-filled pad.

The injury has been reported several times by inspectors of the food products inspection service of the Bureau of Agricultural Economics, United States Department of Agriculture, usually on pears of the Winter Nelis, Bosc, and P. Barry varieties, all of which show more or less russeting of the skin. It has never been found on smooth-skinned pears, although a dark discoloration on pears of the Anjou variety, the result of bruising or rubbing against the paper liner or against other pears, has sometimes been confused with it. A similar injury caused by bruising or rubbing is frequently found on pears of the Bosc variety.

PRELIMINARY EXPERIMENTS

Analyses made in 1926 by T. D. Jarrell, of the Bureau of Chemistry and Soils, United States Department of Agriculture, from pieces of liner material that had been in contact with affected pears, showed the presence of about 1 percent of sodium silicate. A solution obtained by water extraction of pieces of the liner had a definite alkaline reaction. It seemed probable, therefore, that the spotting was caused by the sodium silicate, which had been used as a binder to

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hold the two parts of the corrugated paper together. In order to test this, small pieces of absorbent cotton were dipped in one fourth, one half, and 1 percent solutions of sodium silicate; most of the solution was squeezed out, and the cotton was then laid on unspotted portions of affected Winter Nelis pears. After the fruit had been held in a moist chamber for 24 hours, spots like those originally noted on the pears were found under all the cotton that had been moistened with a silicate solution. Similar spots were produced within 24 hours when moistened pieces of the liner were laid on other pears of the same lot. No discoloration was found under cotton moistened with dis-

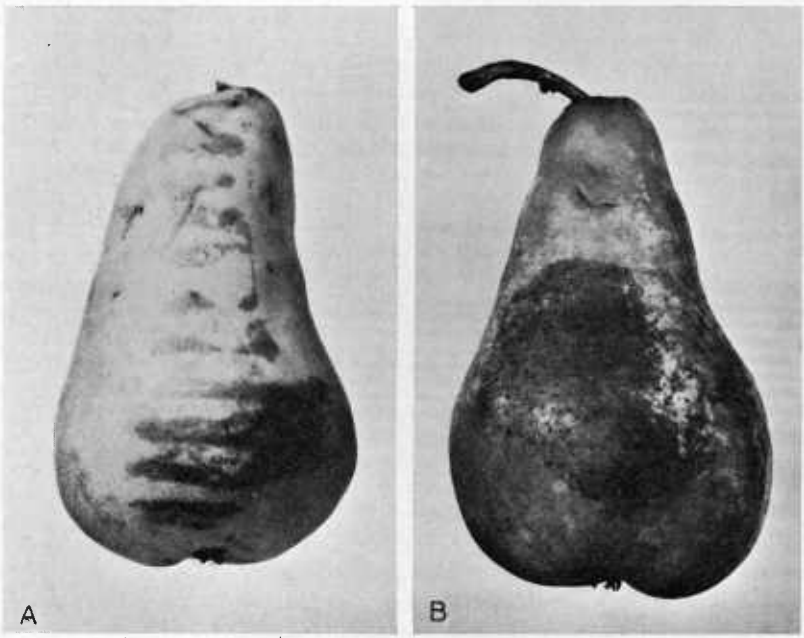

FIGURE 1.—A, Discoloration on a Bosc pear that was in contact with a corrugated paper liner in a commercial shipment. B, Injury produced on a Bosc pear by a 0.1 N solution of sodium hydroxide. This injury was similar to that produced by corrugated-paper liners and alkaline solutions of sodium silicate.

tilled water. It was observed at this time that in all cases the browning was most pronounced on russeted areas.

LATER EXPERIMENTS

After these preliminary investigations no further work was done on the problem until the winters of 1929–30 and 1930–31, when an extensive series of tests was made with six varieties of pears. Seventeen samples of corrugated paper from several sources, 1 sample of excelsior-filled pad, and 5 grades of sodium silicate were used in the tests.

VARIETIES OF PEARS USED

The varieties of pears used in the investigations were P. Barry, Winter Nelis, Bosc, Clairgeau, Bartlett, and Anjou, all of which were grown in Oregon or California. A considerable portion of the skin of P. Barry, Winter Nelis, and Bosc is covered with russet, some speci-

mens being entirely russeted. Clairgeau is a smooth-skinned variety, but the lenticels are conspicuously russeted. Bartlett and Anjou are smooth-skinned, although some specimens of the latter have a russeted area around the blossom end. The region in which the fruit was grown made no significant difference in the results obtained.

No attempt was made to duplicate all conditions with all varieties. Winter Nelis received all treatments. Fruit of the Bosc and Anjou varieties was subjected to most of the test conditions. Bartlett and Clairgeau were used with a few of the paper liners and silicate solutions; P. Barry was used with the paper liners only.

SODIUM SILICATE SOLUTIONS

The five brands of sodium silicate (A, B, C, D, and E) were made up in solutions of five different strengths, namely, 0.1, 0.5, 1, 5, and 10 percent. To test the effect of these, a piece of absorbent cotton about 1 inch square was moistened with the solution and placed on the fruit. The fruit was then placed in moist chambers and most of it was held for 15 days at 40° F. A few lots were held at 32° and 70° to 80° for various lengths of time.

Table 1 shows typical results obtained with solutions of sodium silicate on Winter Nelis, Bosc, and Anjou pears held at 40° F. for 15 days after treatment. The injury consisted of a brown spotting similar to that observed on affected fruit on the market.

TABLE 1.—*Injury produced by various solutions and brands of sodium silicate on pears of three varieties held at 40° F. for 15 days*

Variety	Brand of sodium silicate	Injuries produced by indicated concentrations of sodium silicate solution					
		0.5 percent		1 percent		5 percent	
		Pears	Injury	Pears	Injury	Pears	Injury
		Number		*Number*		*Number*	
Winter Nelis	A	4	None	2	Both moderate	4	All severe.
	B	4	3 severe, 1 moderate.	4	2 severe, 2 moderate.	4	Do.
	C	4	3 moderate, 1 slight.	4	All severe	4	Do.
	D	3	2 moderate, 1 none.	4	2 moderate, 2 slight.	4	Do.
	E	4	1 moderate, 3 slight.	3	All moderate	4	Slight.
Bosc	B	3	1 slight, 2 none	4	3 severe, 1 moderate.	4	All severe.
	C	3	do	4	None	4	Do.
	E	4	None	4	2 slight, 2 none	4	Do.
Anjou	B	4	do	4	None	4	2 none, 2 severe on russeted portion only.
	C	4	do	4	do	4	1 none, 3 trace on russeted portion only.
	E	4	do	4	3 none, 1 trace on russeted portion.	4	None.

Solutions of the E brand silicate only were used on the Clairgeau variety. The only injury was a slight discoloration on a russeted fruit, caused by the 5 percent solution.

None of the solutions used had any effect on Bartlett pears at room temperature, about 70° F. No tests were run at other temperatures.

All the concentrations of sodium silicate solutions of each of the five brands were used with Anjou, Winter Nelis, and Bosc pears at room temperature and with Winter Nelis and Anjou at 32° F. No injury was produced on Anjou, and the results with Winter Nelis and Bosc were similar to those shown for these varieties in table 1.

A few drops of each of the five brands of undiluted sodium silicate were poured out on watch glasses and the fruit was placed directly in this liquid. The result was a brown to almost black injury of the skin and flesh, which was severe on Winter Nelis pears and somewhat

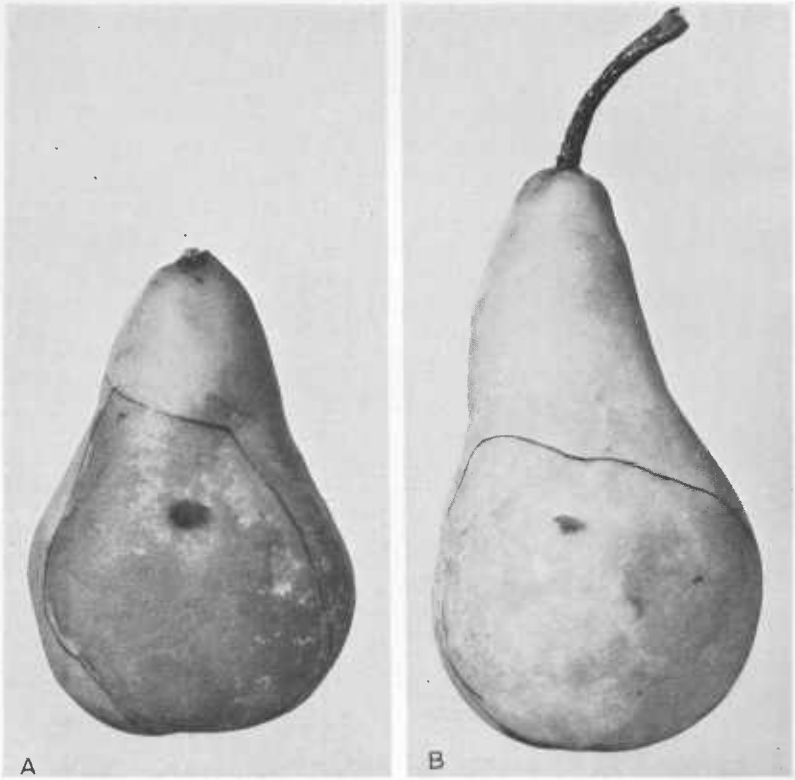

FIGURE 2.—Bosc pears treated with 5 percent sodium silicate: A, Silicate solution not neutralized; B, silicate solution neutralized with sulphuric acid. Areas that were in contact with test solutions are outlined by dark lines.

less so on Anjou. In some cases the discoloration extended into the flesh for a quarter of an inch.

The alkalinity of the various sodium silicate solutions was determined by titrating a 1 percent solution with sulphuric acid, methyl orange being used an an indicator. The results are presented in table 2.

The results of the tests just described furnished some evidence that the discoloration was caused by free alkali in the solution. To obtain further information on this point, enough sulphuric acid was added to the various solutions of sodium silicate used to just neutralize them to methyl orange. The neutralized sodium silicate solutions were

used in the same concentrations, on the same varieties, and under the same conditions as the alkaline sodium silicate solutions previously described. Although the unneutralized solutions caused some injury in concentrations as low as 0.5 percent, and in most instances severe injury to certain varieties, in concentrations of 5 percent the neutralized solutions produced no injury on any of the fruits (fig. 2).

TABLE 2.—*Approximate percentage of alkalinity of sodium silicate solutions*

Alkali calculated as NaOH, using figures obtained by titrating silicate solutions with 0.1 N H_2SO_4; indicator, methyl orange]

Brand of sodium silicate	0.1 percent solution	0.5 percent solution	1 percent solution	5 percent solution	10 percent solution	Undiluted (calculated)
A	0.02	0.10	0.21	1.05	2.09	20.9
B	.037	.18	.37	1.83	3.67	36.7
C	.015	.08	.15	.76	1.53	15.3
D	.016	.08	.16	.81	1.62	16.2
E	.027	.14	.27	1.37	2.74	27.4

SODIUM HYDROXIDE SOLUTIONS

In order to obtain additional information on the relation of alkalinity to the injury, solutions of sodium hydroxide were applied to pears by means of absorbent cotton in a manner similar to that described for sodium silicate solutions. The results obtained at 40° F. are shown in table 3. The injury produced could not be distinguished from that produced by the sodium silicate solutions, paper liners, or the seams of excelsior-filled pads (fig. 1, B). Dilute acid solutions produced typical acid injury, which was easily distinguished from the injury caused by alkali.

TABLE 3.—*Injury produced by solutions of sodium hydroxide of different normalities on pears of four varieties held at 40° F. for 15 days*

Normality of solution	Winter Nelis		Bosc		Anjou		Clairgeau	
	Pears	Injury	Pears	Injury	Pears	Injury	Pears	Injury
	Number		*Number*		*Number*		*Number*	
0.3 N (1.2 percent)	4	Very severe.	4	2 severe, 2 moderate.	------	----------	3	Slight on russet portion only.
.2 N (0.8 percent)	4	Severe	3	Moderate	4	Slight on russet portion only.	------	
.1 N (0.4 percent)	4	do	4	2 severe, 2 moderate.	4	None	3	2 none, 1 trace on russet portion only.
.03 N (0.12) percent	4	2 severe, 2 moderate.	2	1 severe, 1 trace.	4	do	3	None.
.01 N (0.04 percent)	4	do	4	1 trace, 3 none.	------	----------	------	

EXCELSIOR-FILLED PADS

Excelsior pads covered with paper are used to some extent in pear boxes as a protection against bruising, especially with tender varieties. The edges of the paper are lapped and fastened together with an

adhesive, usually sodium silicate, and the seams thus made may cover a quarter of the area on one side of the pad.

Moistened pieces of these seams produced injury on Bose, Winter Nelis, and P. Barry pears (fig. 3, B). This injury was similar to, but usually more severe than, that produced by paper liners. The alkalinity of the seam, determined as previously described for the paper liners, was 2.35 percent, calculated as NaOH. A water extract of the excelsior caused no discoloration of the pear skin.

CORRUGATED-PAPER LINERS

Pieces of corrugated-paper liners about 1½ inches square were moistened with distilled water and placed in moist chambers and pears were laid on them. Only enough water was used to make the

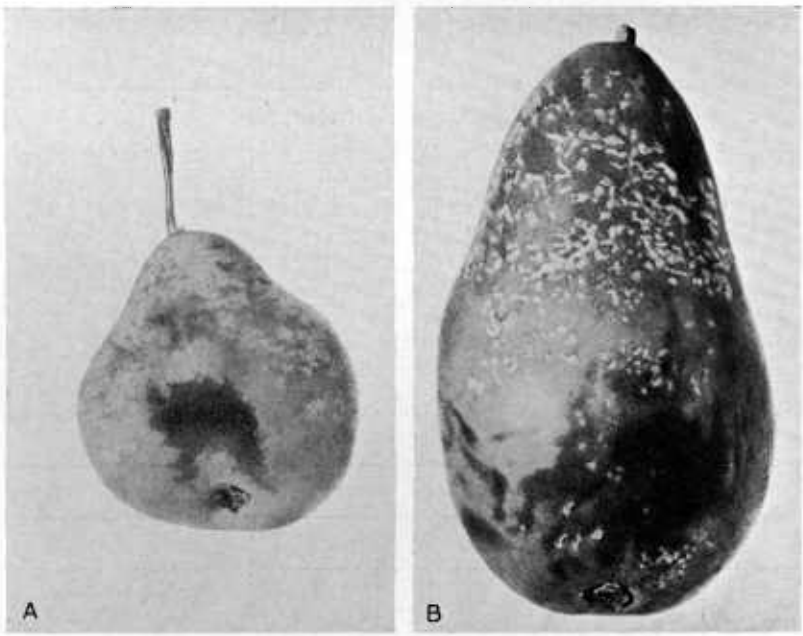

FIGURE 3.—A, Discoloration on a Winter Nelis pear, produced by placing it in contact with a moist section of corrugated-paper liner; B, P. Barry pear taken from a commercial shipment of pears in Chicago, showing discoloration on the portion that lay in contact with an excelsior-filled pad the seams of which contained sodium silicate.

paper moist, in order to avoid the possibility of washing out any soluble substances that the paper might contain.

The alkalinity of the various corrugated papers was determined as follows: A piece of each paper, containing about 12 to 15 square inches, was weighed and then placed in distilled water for 24 hours. The resulting solution was then titrated with 0.1 normal sulphuric acid, methyl orange being used as an indicator. The alkalinity by weight was calculated as sodium hydroxide.

The amount of discoloration caused by different samples of corrugated-paper liners at 40° F. is given in table 4. The duration of the treatment was 15 days.

TABLE 4.—*Discoloration produced on pears of 4 varieties by contact with corrugated-paper liners for 15 days at 40° F.*

Paper liner no.	Adhered with—	Alkalinity expressed as NaOH	Winter Nelis		Anjou		Bosc		Clairgeau	
			Pears	Injury	Pears	Injury	Pears	Injury	Pears	Injury
		Percent	*Number*		*Number*		*Number*		*Number*	
1	Sodium silicate	0.91	4	1 none, 3 moderate	4	None	3	1 severe, 2 moderate		
2	Flour dextrin paste	.08	4	None	4	do			3	None.
3	do	.09	4	do	4	do	3	None		
4	Sodium silicate	1.06	4	Trace	4	do	3	Moderate		
5	do	.83	4	2 severe, 2 moderate	4	3 none, 1 moderate on russet portion only.	3	do		
6	do	1.22	3	2 severe, 1 trace	4	None	3	Slight		
7	do	.53	3	do			3	None		
8	do	.82	3	1 none, 1 moderate, 1 severe.	4	None	3	do		
9	do	.49	4	2 none, 1 trace, 1 moderate.						
10	do	1.43	4	1 trace, 3 moderate	4	None	3	None		
11	do	.79	4	3 none, 1 trace	4	do				
12	do	1.60	4	1 moderate, 3 severe	4	do	3	Moderate	3	None.
13	do	.76	4	None	4	do	3	None		
14	Flour dextrin paste	.05	4	do	4	do				
15	Sodium silicate	.73	4	3 trace, 1 moderate	4	do				
16	do	.76	4	3 moderate, 1 severe	4	3 none, 1 trace on russet portion only.	3	Trace	3	2 none, 1 slight on russet portion only.
17	do	.63	4	Severe	4	None	3	do		
Check	Moist filter paper		4	None	4	do	4	None		

Results similar to those given in table 4 were obtained with Anjou, Winter Nelis (fig. 3, A), and Bosc pears at room temperature (about 70° F.), and with Winter Nelis and Anjou at 32°. Discoloration was produced on P. Barry with paper liner no. 6 at room temperature. None of the papers used produced injury on Bartlett pears.

MOISTURE

To test the effect of moisture in the package during the storage period, Winter Nelis pears were packed in two standard pear boxes with a paper liner that had been found to cause discoloration. The liner in one box was moistened; that in the other box was left dry. About one half of the pears in each box were wrapped in ordinary fruit wrappers. Both boxes were then left at 32° F. for 42 days, after which they were examined. The results are given in table 5.

TABLE 5.—*Effect of moisture in the discoloring of Winter Nelis pears by paper liners, during a storage period of 42 days at 32° F.*

Packing conditions	Pears	Effect on pears at area in contact with paper liners
Liner moist:	*Number*	
Pears wrapped	14	All badly discolored.
Pears unwrapped	13	All badly discolored, slightly more than in wrapped fruit above.
Liner dry:		
Pears wrapped	14	None.
Pears unwrapped	14	1 pear discolored.

REMOVAL OF SPOTTING WITH HYDROCHLORIC ACID

The spotting produced by paper liners was almost completely removed from Winter Nelis pears by allowing the fruit to remain in a 1 percent solution of hydrochloric acid for 1 hour. No apparent removal of the spotting was noticed after 24 hours when pears were placed in water alone.

DISCUSSION OF RESULTS

The typical brown discoloration that has been observed on the market and described earlier in this paper was produced experimentally on russeted varieties of pears by seams of excelsior-filled pads and by corrugated-paper liners when sodium silicate was used as an adhesive. This injury was also produced on russeted pears by solutions of sodium hydroxide and commercial sodium silicate. The injury was not produced by corrugated-paper liners in which flour-dextrin paste had been used as the adhesive instead of sodium silicate. Each of the corrugated-paper liners in which sodium silicate had been used as an adhesive produced the discoloration at least once on either Winter Nelis or Bosc pears during the series of tests.

EFFECT OF RUSSETING

The injury produced seems to be associated with the russeting on the fruit. The sodium silicate solutions, corrugated-paper liners, excelsior-filled pads, and sodium hydroxide solutions produced injury in these experiments on the russeted varieties, namely, Bosc,

Winter Nelis, and P. Barry. The injury on these varieties was most severe on the more heavily russeted fruit. Practically no injury was produced on the smooth-skinned varieties, although a small amount of discoloration was sometimes produced on the russeted areas of Clairgeau and Anjou pears. As heretofore mentioned, the discoloration has never been noticed on the market on smooth-skinned varieties.

Russeting results from a cracking and weathering of the epidermis and an increased development of the corky parenchyma beneath.[2] Fruit russeted as a result of frost injury wilts rather rapidly,[3] which indicates that the skin of a russeted fruit is more permeable to water or water vapor than that of a smooth-skinned fruit.

The brown discoloration on russeted pears probably is caused by the action of the solution on the corky parenchyma or periderm which has been exposed by the disappearance of the epidermis, although it may result from the penetration of the solution into a few layers of cells of the flesh.

EFFECT OF ALKALINITY

The discoloration noted on pears in the various experimental lots of fruit and on those observed on the market had very much the appearance of plant tissues browned by ammonia or other alkalies. It seemed possible, therefore, that the browning produced when certain varieties of pears come in contact with corrugated paper put together with sodium silicate might be caused by free alkali in the silicate. The results of the experimental work described herein make it apparent that the brown discoloration is actually caused in this way. The following facts form the basis for this conclusion:

Although solutions of sodium silicate, in some cases in concentrations as low as 0.5 percent, produced injury, no injury was produced in any case when these solutions were neutralized, even when a 10 percent solution of the silicate was used.

Typical brown discoloration was produced by solutions of sodium hydroxide in concentrations as low as 0.01 N (0.04 percent).

Only the samples of corrugated-paper liners and the seams of excelsior-filled pads that contained sodium silicate produced the discoloration. These were of high alkalinity as compared with the corrugated pads in which some other adhesive was used and by which no discoloration was produced.

Although not conclusive in itself, the removal of the discoloration by a 1 percent solution of hydrochloric acid gives further evidence that the discoloration is due to alkalinity.

EFFECT OF MOISTURE

The humidity within a box of pears is probably high enough at times to cause some of the sodium silicate contained in corrugated-paper liners or the seams of excelsior-filled pads to go into solution and thus be carried to the skin of the fruit, where it produces the discoloration. The moisture probably results largely from condensation produced by the changes in temperature to which boxes of pears are normally subjected. Probably some moisture is also given off by the fruit itself.

HYDROLYSIS OF SODIUM SILICATE

It is realized that when enough acid is added to a sodium silicate solution to render it approximately neutral, the condition established

[2] GARDNER, V. R., BRADFORD, F. C., and HOOKER, H. D. THE FUNDAMENTALS OF FRUIT PRODUCTION. 686 p., illus. New York. 1922.

[3] PADDOCK, W., and WHIPPLE, O. B. FRUIT GROWING IN ARID REGIONS; AN ACCOUNT OF APPROVED FRUIT-GROWING PRACTICES IN THE INTER-MOUNTAIN COUNTRY OF THE WESTERN UNITED STATES. 395 p., illus. New York. 1914.

is probably not permanent because of the hydrolysis of the silicate and the setting free of more alkali in the solution.[4] The extent of this hydrolysis was evidently small, however, during the course of these tests. The fact that solutions of sodium silicate or sodium hydroxide produced the discoloration, whereas "neutralized" solutions of sodium silicate did not, is strong evidence that for the duration of the experiments described there was little or no hydrolysis and consequently little or no release of free alkali into the sodium silicate solution after "neutralization."

SUMMARY

A brown discoloration of russeted varieties of pears is described.

The injury was produced experimentally by placing fruits in contact with corrugated-paper liners and the seams of excelsior-filled pads containing sodium silicate, and by applying to the fruits weak solutions of commercial sodium silicate and of sodium hydroxide. Neutralized solutions of sodium silicate and paper liners put together with some adhesive other than sodium silicate did not produce the injury.

Alkaline substances contained in sodium silicates apparently are the direct cause of the injury as it occurs in commercial lots of fruit.

In many cases there is apparently sufficient moisture within boxes packed with pears to cause some of the alkaline substances contained in paper liners put together with sodium silicate to go into solution and produce the injury.

[4] BOGUE, R. H. THE HYDROLYSIS OF THE SILICATES OF SODIUM. Jour. Amer. Chem. Soc. 42: 2575–2582. 1920.