INFLUENCE OF ALUM ON THE FIRMNESS OF FRESH-PACK DILL PICKLES

INTRODUCTION

ALUM has been used in the manufacture of pickle products for many years, and no one seems to know how the practice originated (Fabian and Krum, 1949). When alum is added during processing (= desalting of brine-stock) or to finished pickle products made from fermented, salt-stock pickles, such as processed dills or sweets, it is reported to play an important role in making the cucumber pickles more crisp and firm. With the development of nonfermented-type products, known as fresh-pack or pasteurized pickles (Etchells, 1938; Etchells and Jones, 1942, 1944), most manufacturers added alum to these products as well. Fresh-pack products, both dill and sweets, have made substantial gains in consumer acceptance, and now, after approximately 35 years from the time of their introduction, they require more than 40% of the national crop of pickling cucumbers (Monroe et al., 1969). In research designed to improve procedures for preparation of pasteurized pickle products, Etchells and Jones (1942, 1944) discussed in detail the methods of manufacturing high-quality products. The addition of alum was not a part of their procedure; nevertheless, they reported that most of the original cucumber crispness or firmness was retained for about 8 months for fresh-pack sweet slices and whole dill pickles; and, for 16 months for fully fermented genuine dills. The basic pasteurization procedure they described was developed under commercial conditions, and was readily adaptable to either hot water or steam as the heating medium. An internal product temperature of at least 160°F, but not over 165°F, maintained for 15 min was called for, followed by prompt cooling of the product to below 90°F. The equilibrated acid content of the various products covered by Etchells and Jones ranged from 0.4–1.7% acetic (= 4 to 17 grains vinegar).

We found no reports in the literature demonstrating the value of alum in the manufacture of fresh-pack pickle products. The research reported here represents a series of experiments on the firmness of fresh-pack dill pickles carried out over a 3-yr period at a pickling plant located in Ohio, with parallel studies being done in our Raleigh laboratory. The experiments were designed to give prime consideration to the influence of alum [$Al_2(SO_4)_3 \cdot 18H_2O$], together with different acidity levels of either lactic and/or acetic acids on the firmness of whole cucumbers (unspiced) or whole dill pickles, prepared and pasteurized under both laboratory and commercial conditions.

MATERIALS & METHODS

Laboratory experiments

The four alum salts tested (aluminum potassium sulfate, aluminum ammonium sulfate, aluminum sodium sulfate and aluminum sulfate) were all certified, reagent-grade chemicals. The acidic properties of each alum salt were determined by preparing a series of quantitative aqueous solutions (0.05, 0.10, 0.15, 0.20, 0.25 and 0.30% weight/volume, based upon the actual amount of alum salt rather than the hydrated salt, and titrating 10-ml samples of each with 0.111N sodium hydroxide solution to an endpoint of pH 7.5, measured with a Beckman Zeromatic pH meter. The acidity of each alum salt solution is expressed in milliequivalents (meq) per gram of alum salt. Acetic and lactic acids were of reagent-grade and the concentration of each acid was determined by titrating a 10-ml sample with 0.111N sodium hydroxide to pH 7.5. The Kosher-style, dill pickle cover-brine was obtained from a local pickle manufacturer and represented their regular formula. The sodium chloride content of the samples was determined by a method previously described (Etchells et al., 1964).

Cucumbers, Model variety, size 1-1/8 to 1-3/8 in. diam were packed into 32-oz (1-qt) glass jars so as to maintain close to 60% cucumbers and 40% cover-brine on a weight basis. To obtain this pack-out ratio, each jar contained 12–15 cucumbers weighing 550–560g. The jars were then covered with about 370 ml of the appropriate test brine, leaving headspace of approximately 1/4 in. Next, the jars were closed with 70 mm, 4-lug, "twist-off" caps (White Cap Co., Chicago, Ill.) and pasteurized in a hot-water bath by the method described earlier (Etchells and Jones, 1944). All jars were stored at room temperature (about 78°F).

Experiments at the pickle company

Fresh-pack (pasteurized) dill pickles were made during three growing seasons at the cooperating pickle plant; 350 quart samples of pickles were hand-packed and represented 98 different treatments as to amounts of acetic and/or lactic acids and with or without the addition of alum. The cucumber variety, SMR-15, was used, and the sizes ranged from 1 to 1-3/8 in. diam (commercial sizes 1A and 1B). The packing, capping, pasteurizing, storing and testing of the finished products were essentially the same as that described for the laboratory experiments. One difference was that these were machine-capped and pasteurized in a commercial steam unit to an internal-product temperature of 165°F (held for 15 min) followed by water-spray cooling to about 90°F.

Product evaluation

The procedure used for cucumber pickle evaluation and for brine analyses of each treatment was that used by Monroe et al. (1969). At the time each jar was opened, the following physical and chemical measurements

Table 1—Formulae and acidic properties of commercial alum salts

Chemical name	Trade name	Formulae[a]	Acidic properties of 0.1% aqueous solution[b] pH	Meq as acid/g
Potassium aluminum sulfate	Potassium alum Alum meal Alum flour	$KAl(SO_4)_2 \cdot 12H_2O$	3.89	10.5
Ammonium aluminum sulfate	Ammonium alum	$NH_4Al(SO_4)_2 \cdot 12H_2O$	3.85	12.9
Sodium aluminum sulfate	Soda alum	$NaAl(SO_4)_2 \cdot 12H_2O$	3.75	14.8
Aluminum sulfate	Cake alum Patent alum	$Al_2(SO_4)_3 \cdot 18H_2O$	3.74	16.5

[a]Formulae of the first three alum salts listed in the table are sometimes written as double salts. e.g., $Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$.
[b]Alum salt solutions prepared on weight of each salt less water of crystalization

were made: (1) visual signs of spoilage as indicated by turbidity of the brine and gas pressure; (2) product odor; (3) brine acidity as acetic or lactic; (4) brine pH; (5) NaCl content of brine; and (6) pickle firmness in pounds as measured by the USDA Fruit Pressure Tester (Magness and Taylor, 1925). The firmness rating in pounds was the average value for 10 cucumbers each receiving a center punch, using a 5/16 in. diam plunger tip. The firmness rating scale follows: 18 lb and above = very firm; 17–14 = firm; 13–11 = inferior; 10–5 = soft; 4 and below = mushy (Bell et al., 1955).

RESULTS & DISCUSSION

Acidic properties of the different alum salts

There has been little or no information published on the acidic properties of the alum salts or their influence on the pH of pickle products. Fabian and Krum (1949) listed four alum salts used in the manufacture of pickle products. These are shown in Table 1 together with their formulae and acidic properties as determined in the laboratory. By definition, the most acidic alum, aluminum sulfate, is not a "true alum." Chemically, an alum is a combination of a monovalent and trivalent ion salt with 12 or 24 molecules of water of crystallization (Fabian and Krum, 1949). Aluminum sulfate is known as "cake alum" or "patent alum" according to the Merck Index, 8th Edition (1968) and it is accepted and used as alum in the manufacture of pickle products. Over the years, the food industry, and especially the pickle industry, has added aluminum sulfate to their products. For this reason, the experiments reported herein used aluminum sulfate.

To determine the acidic properties of aluminum sulfate, increasing levels of this salt were added to distilled water, and to a commercial Kosher-style dill pickle cover-brine. Increasing concentrations of alum (Table 2) in distilled water decreased the pH very markedly. As mentioned earlier, 0.1% (1g/liter) of alum, which is the amount normally used by the industry for pickle products, gave a pH value of 3.74 and 16.5 meq per gram in distilled water. This is equivalent to 0.0165N acid. To theoretically express 0.1% alum acidity as an equivalent to acetic acid, the following calculations are used:

(1) 1 meq acetic acid = 60 mg
(2) 1g alum = 16.5 meq as acid
(3) to express alum acidity as grams of acetic acid, 1g alum = 16.5 meq as acid x 60 mg of acetic acid = 990 mg = 0.99g of acetic acid
(4) thus, 1g alum has approximately the same acidity as 1g acetic acid.

Table 2 also presents the titratable acidities expressed as acetic and the pH values of a Kosher-style dill pickle brine equilibrated with increasing levels of alum in 1-qt jars with and without cucumbers. The dill pickle brine without cucumbers, but with increasing concentrations of alum, decreased the pH values (3.38 to 3.09) together with an increase in acidity as acetic (0.59 to 0.92%). The acetic acid increased about 0.11% with each 0.1% of alum added; this confirms the alum-acetic acid equivalents calculated above. When cucumbers were covered with the Kosher-style dill pickle brine containing the different alum levels, the cucumbers showed buffering effect, particularly at the lower alum levels (Table 2). This confirms earlier observations (Etchells and Moore, 1971).

Alum-treated, pasteurized cucumbers

The results of laboratory tests on four experimental packs of pasteurized cucumbers, acidified with acetic or lactic acid, each with and without alum are given in Table 3. As previously determined, the concentrations of the two acids needed in the cover-brine to equilibrate at pH 3.8–4.0 were 5.0% acetic and 1.0% lactic. The addition of alum lowered the pH, increased the acidity and reduced pickle firmness. Acetic acid without alum was the only treatment wherein the pickles remained firm after 8 months' storage.

Experiments at a pickle plant on fresh-pack dill pickles

The influence of different levels of lactic and/or acetic acids, with and without alum, on the firmness of fresh-pack dill pickles is given in Table 4. After 10 months' storage at room temperature, the experimental pack was examined. The pH values of the equilibrated cover-brines reflected the ionization behavior for the acids used and the alum-treated lots depressed the pH in all cases. This pH difference was more noticeable at the lower acid concentrations. Cucumber firmness was markedly reduced by the use of alum and was directly related to

Table 2–pH and titratable acidity of alum in water and in a Kosher-style dill pickle brine

Alum added to equilibrate at	Distilled water		Kosher-style pickle brine[a] Without cucumbers		With cucumbers	
%	pH	meq/g	pH	Acid as acetic %	pH	Acid as acetic %
0.00	6.38	0.0	3.38	0.59	3.88	0.67
0.05	3.89	8.9	3.31	0.64	3.75	0.72
0.10	3.74	16.5	3.25	0.71	3.57	0.74
0.15	3.65	26.2	–	–	3.37	0.75
0.20	3.58	35.1	3.14	0.82	3.26	0.77
0.25	3.52	44.6	–	–	3.17	0.78
0.30	3.43	52.1	3.09	0.92	3.12	0.80

[a]The cover-brine contained 1.47% acetic acid, pH 3.25 and 7.0% NaCl. The tests were carried out in 1-qt jars with cucumbers (1-1/8 to 1-3/8 in. diam) or water to replace cucumbers representing 60% of the total weight in each jar. Data shown are averages of duplicate treatments. Equilibration time was 48 hr.

Table 3–Influence of alum on pasteurized cucumbers acidified with acetic or lactic acids after 4 and 8 months' storage periods

Treatment of cucumbers[a] (desired acidity at equilibration)	Brine analysis after storage[b] pH	Acidity %	Cucumber firmness (pressure test) at storage periods of 4 months lb	4 months rating	8 months lb	8 months rating
Acetic acid						
2.0%, No alum	3.84	2.11	15.8	Firm	14.3	Firm
2.0%, 0.1% alum	3.74	2.18	12.5	Inferior	11.1	Inferior
Lactic acid						
0.4%, No alum	3.95	0.52	15.3	Firm	13.2	Inferior
0.4%, 0.1% alum	3.82	0.61	11.8	Inferior	12.0	Inferior

[a]Model variety cucumbers, 1-1/8 to 1-3/8 in. diam were covered with the test brine containing the acids. 5 ml of alum solution (18.5g/100 ml) was added to each quart of the alum-treated lots.
[b]Brine analyses for pH and acidity (expressed as g/100 ml of each organic acid) are averages of duplicate brine samples at 4 and 8 months' storage periods. NaCl content 2.0%

the quantity of acid in the cover-brine. The striking effect of the influence of alum on the reduction of pickle firmness in lots acidified with different levels of lactic acid is shown in Figure 1. The increase in brine acidity and resultant decrease in brine pH caused by the additive (alum) is also clearly shown. Also, increasing levels of acid resulted in loss of pickle firmness.

The influence of different levels of alum, together with different levels of acetic and lactic acids, on the quality of fresh-pack dill pickles is presented in Table 5. Many of the low acid treatments showed microbial spoilage even though the pasteurization procedure was the same in all cases. However, as the amount of alum increased within each acid concentration, there was a number of jars of pickles that were preserved. For example, in Series I, Experiment 1, Treatments B and C, the control jars spoiled, but those with alum did not. The most noticeable deterioration in pickle firmness occurred with the high concentrations of lactic acid. The acetic acid treatments without alum (Table 5, Series II) were not free of microbial spoilage until the amount of acid added reached 9 ml per quart (0.73% when equilibrated). This is in agreement with Monroe et al. (1969) who recommended a minimum of 0.6% acetic acid for acidification of fresh-pack dill pickles. The addition of alum in every case—where spoilage was not a factor—resulted in a clear-cut loss in pickle firmness.

It should be apparent from the results described here that the continued use of alum in fresh-pack products by pickle manufacturers will continue to produce pickles of inferior quality as to firmness. The industry must remember that the alum in their products represents about 0.10% titratable acidity (calculated as acetic) and exerts a corresponding depression of the brine pH. Thus, with a new, nonalum formula, the proper acidification at equilibration with the cucumbers, should be sufficient to produce a brine pH below 4.0.

Based on findings by Monroe et al. (1969), Etchells and Moore (1971), as well as data of the authors (Table 2) a fresh-pack cover-brine for medium-size, whole dills containing 1.7–1.8% acetic acid, plus 7.2% salt should equilibrate, with the water content of the cucumbers, close to 0.65–0.70% acetic acid, about 2.8% salt and with a brine pH between 3.8 and 4.0. These figures are based on quart jars of pickles, packed so as to maintain 65% pickles and 35% brine. For a slightly looser pack—with 60% pickles—(which may be closer to the conventional machine-packs of industry today) the values cited for equilibrated acidity and salt content would be slightly higher, but the pH values should still fall in the range pH 3.2–4.0, never above pH 4.0.

In addition to the acidity adjustment discussed for a nonalum, fresh-pack formula, the packer should be aware of a similar need resulting from the greater buffering capacity of small-sized cucumbers (7/8 to 1-1/8 in. diam) as compared to the larger-sized fruit (1-1/2 to 2 in. diam). To compensate for this property, the cover-brine formulation for small-sized, fresh-pack pickles such as whole dills will require about 0.15–0.25% more acidity (calculated as acetic acid) than that used for large cucumbers.

In the interest of avoiding spoilage of fresh-pack products, the plant operator should be very careful when making any changes in his basic pasteurization procedure as well as any revisions of product

Table 4—Brine pH and cucumber firmness of fresh-pack dill pickles acidified with lactic and/or acetic acids, with and without alum, examined after 10 months' storage

	Acid treatments		No alum added		Alum added[b]		Cucumber firmness reduced by addition of alum
Code	Added per qt[a] ml	Equilibrated %	Brine pH	Cucumber firmness (PT)[c] lb	Brine pH	Cucumber firmness (PT)[c] lb	lb
Series I, lactic acid							
A	1.5	0.14	4.24	13.5	3.93	12.2	1.3
B	2.0	0.18	4.02	14.2	3.80	12.2	2.0
C	2.5	0.22	3.85	13.8	3.67	12.7	1.1
D	3.0	0.27	3.79	12.5	3.61	11.7	0.8
E	4.0	0.36	3.66	12.0	3.48	11.0	1.0
F	5.0	0.45	3.45	12.2	3.32	11.2	1.0
G	6.0	0.54	3.32	11.5	3.30	9.7	1.8
Series II, acetic acid							
A	1.00	0.08	4.68	13.5	4.24	13.5	0.0
B	1.33	0.11	4.52	13.8	4.18	13.8	0.0
C	1.67	0.14	4.42	15.0	4.15	13.2	1.8
D	2.00	0.16	4.36	13.0	4.14	12.0	1.0
E	2.67	0.22	4.27	13.0	4.07	12.2	0.8
F	3.33	0.27	4.14	14.2	3.94	10.5	3.7
G	4.00	0.32	4.05	13.8	3.88	11.2	2.6
Series III, lactic/acetic mixture							
A	0.75/0.50	0.07/0.04	4.48	13.2	4.12	13.0	0.2
B	1.00/0.67	0.09/0.05	4.30	14.2	4.05	14.0	0.2
C	1.25/0.83	0.12/0.07	4.18	14.2	3.92	13.7	0.5
D	1.50/1.00	0.14/0.08	4.12	13.2	3.89	12.2	1.0
E	2.00/1.33	0.18/0.11	3.89	14.5	3.66	13.5	1.0
F	2.50/1.67	0.23/0.14	3.78	13.8	3.60	13.5	0.3
G	3.00/2.00	0.27/0.16	3.66	14.0	3.49	11.7	2.3

[a] As 85% lactic or 85% acetic acid. Cover-brine was an "Overnight Dill" formula containing 7% salt. Equilibrated salt ranged 2.9–3.0%

[b] Alum as $Al(SO_4)_3 \cdot 18\ H_2O$ added in cover-brine at 0.2% (equiv. 0.75g/qt) and calculated to equilibrate at 0.08%

[c] Pressure test values in pounds; values shown are averages of the center punch for 10 cucumbers, size 1-1/8 to 1-3/8 in. diam. Data shown are averages of duplicate samples within each treatment.

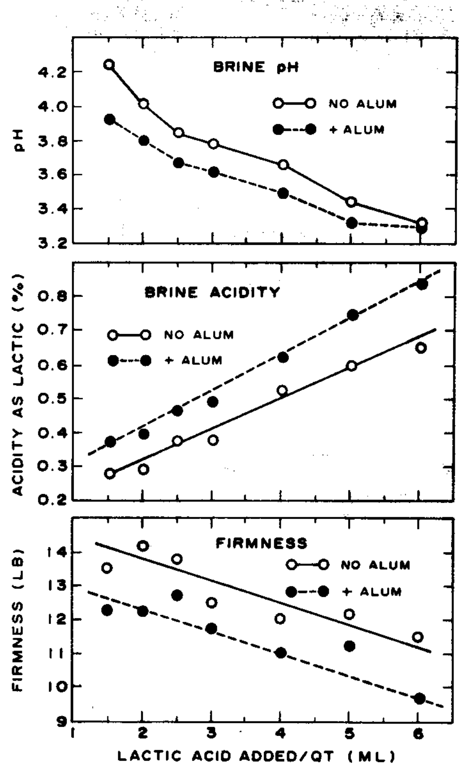

Fig. 1—Influence of alum on the reduction of pickle firmness in lots acidified with different levels of lactic acid.

Table 5—The effect of different levels of alum, acetic and lactic acids on cucumber firmness and microbial spoilage of fresh-pack dill pickles after about 12 months' storage.

	Acid treatments		Alum added (g per quart jar)[b]					
	Added per qt[a]	Equilibrated	0.00	0.25	0.40	0.75	1.10	1.67
			Cucumber firmness in pressure test values[c]					
Code	ml	%	lb	lb	lb	lb	lb	lb
Series I, lactic acid								
Experiment 1, low levels								
A	0.5	0.04	11.5(S)	–	11.9(S)	11.7(S)	10.8(S)	–
B	1.0	0.09	10.0(S)	–	12.8	12.0	13.2	–
C	1.5	0.14	12.7(S)	–	13.3	12.4	13.0	–
D	2.5	0.22	12.6	–	13.0	12.8	12.6	–
Experiment 2, high levels								
E	2.25	0.20	4.2(S)	6.4(S)	–	11.4(S)	–	10.6
F	6.75	0.61	11.4	11.2	–	9.1	–	8.8*
G	13.50	1.22	4.5*	4.2*	–	4.7	–	6.2*
Series II, acetic acid								
Experiment 1, low levels								
A	0.33	0.03	11.0(S)	–	11.4(S)	12.0	10.6	–
B	0.67	0.05	12.2(S)	–	11.6(S)	11.6(S)	––[d]	–
C	1.00	0.08	13.2(S)	–	13.0(S)	12.4	12.0	–
D	1.67	0.14	14.2(S)	–	13.8	12.5	13.4	–
Experiment 2, high levels								
E	1.50	0.12	<3.0(S)	5.2(S)	–	6.2(S)	–	7.8(S)
F	4.50	0.36	7.4(S)	7.4(S)	–	9.8	–	11.4
G	9.00	0.73	10.6	11.6	–	9.8	–	10.4

[a]See Footnote a, Table 4.

[b]Alum as $Al_2(SO_4)_3 \cdot 18\,H_2O$ and added in cover-brine, calculated to equalize as follows: 0.25g/qt = 0.027%; 0.40g = 0.043%; 0.75g = 0.08%; 1.10g = 0.119%; and 1.67g = 0.18%.

[c]Pressure test values in pounds with 5/16 in. tip; values shown are averages for the center punch of 10 cucumbers; sizes used 1 to 1-1/8 in. diam for Exp. 1 and 1-1/8 to 1-3/8 in. diam for Exp. 2. Data shown are averages of duplicate sample. (S) indicates observed spoilage by a cloudy brine and gas pressure on the cap for one or both jars. * indicates brine pH of 3.2 and below. Experiment 1 pickles evaluated after 12 months; Experiment 2 pickles after 13 months.

[d]Jars broken

specifications calling for reduced acidification or lower salt content. For example, arbitrarily reducing the acid and salt content in a fresh-pack product, such as whole dill pickles, to achieve some abnormally mild flavor might inadvertently lead to a very serious spoilage problem and a public health hazard as well. There can be no compromise with the proper acidification and pasteurization procedures in the preparation of high-quality, fresh-pack pickle products.

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