THE COMPARATIVE EFFECT
OF
CATIONS AND ANIONS
ON
THE FIRMING OF BRINED CHERRIES

by

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CHAPTER I

INTRODUCTION

Brined cherries, the raw material for Maraschino type cherries, an important ingredient in canned fruit cocktail and salad is one of the important industries of the North-west. Up to early thirties, brined cherry stocks were almost entirely imported from Italy and France (88). Bullis and Wiegand (17) and Cruess (26) on the west coast are credited with placing this industry on a firm footing and standardizing the procedure of brining.

With cherries, the object, besides preservation against spoilage, is to bleach the fruit to a light straw-color and to harden the tissue, so that the fruit may be pitted, leached, dyed, candied or glaced without becoming soft or mushy and retaining its original shape and be receptive to the syrup. The procedures of brining are given by Bullis and Wiegand (17) and Atkinson and Strachan (2,3,4,5,6).

Skin-cracking and softening following storage of brined cherries are two detriments to quality encountered by the practical briner. He is not only at a loss financially when these conditions occur, but also, he is often at a loss to explain their occurrence in apparently comparable barrels or even in the same barrel, where some cherries are cracked and

soft, whereas others are in good, firm, uncracked condition.

In spite of its industrial importance, unfortunately, very little work has been done, with the exceptions of a few investigators, who, too are of contradictory opinions. The role of pectic substances along with polyvalent ions giving the corresponding pectates and pectinates, is assumed and held responsible for firming of most of the fruits and cherries. No one, however, has published work with cherries to prove the above assumption.

Due to these differences of opinions and also the very unclarified status of pectic substances with respect to nomenclature, methods of determination, and interpretation of results, the bearing of the condition of the fresh fruit either on the tree or the handling procedures on the finished product, this investigation was undertaken to obtain information on some of the problems, especially:

1. The possible interrelationship of the changes which occur in the fruit tissues during the ripening process on the tree, during handling and storage.

2. The changes, which cherries undergo, when they are brined with different firming agents, with particular reference to firming and brine-cracking of these cherries.

3. The comparative effects of various cations and anions on firming and brine-cracking of cherries, using some of the groups in lyotropic or Hofmeister series.

More of calcium salts were used since calcium in small quantities is allowed in fruit products, whereas other heavy minerals are not.

4. The role of pectic substances in the phenomenon of firming and cracking of the brined-cherries.

CHAPTER II

REVIEW OF LITERATURE

Biochemical and Physiological Activities During Ripening and Handling of Sweet Cherries:

Hartman and Bullis (36, pp.1-38) state that the decrease in firmness with ripening is less pronounced in cherries than that manifested by most deciduous fruits. There is a varietal difference to this effect. There is a material increase of sugar and solid content closely correlated with maturity and quality. Specific gravity of the juice and the cherries increases with the ripening period. Although reduction in acidity is not always consistent, acidity decreases as the maturity approaches; pH increases and it varies with varieties. Astringency and tannin contents decrease with maturity and thus improve the quality. Color of cherries gets darker with maturity.

Within the same orchard or even on the same tree, sweet cherries may show considerable variation in degree of maturity, and this variation is marked, depending upon the load on the trees or branches and whether they are growing in singles or in clusters.

During storage, aside from the loss of weight and volume, sweet cherries undergo no striking physiological and chemical changes immediately following removal from the

tree. There is a slight increase in acidity probably due to concentration following transpiration. Temperature and humidity affect the loss of weight and volume; low temperatures and high humidities are beneficial for storage of sweet cherries. At higher temperatures and low humidities, sweet cherries are soft and susceptible to mechanical injury.

Maturity of cherries affects the canning quality as regards flavor, aroma, size, drained weight and texture of the product.

Cracking:

Hartman and Bullis (36, pp.1-38) are of the opinion that cracking results from excessive water absorption either through the root system or through the epidermis of the fruit itself. The fruit is not susceptible to cracking just before it attains prime condition. Osmotic pressure due to increase of sugar and other soluble solids, increases tendency of the fruit to absorb more water. Varietal differences and stages of maturity are important to this effect, in their opinion.

Verner and Blodgett (84, pp.1-14), and Verner (86, pp.54-57; 85, pp.271-274) differ with Hartman and Bullis (36, pp.1-38) and do not hold excessive water absorption by cherries as the cause of their cracking on trees. They hold the following factors responsible for the cracking

of cherries; elasticity of the cell, osmotic concentration
of the juice, turgor of the fruit, temperature of the water
or solution, varietal, local and climatic differences and
the kinds of sprays or treatments employed.

Kertesz and Nebel (43, pp.763-771) attribute cracking
and softness to the size of epidermal and parenchymatous
cells and the varietal differences to this effect. They
suggest that cracking is caused by the forces of the swell-
ing colloids of the flesh rather than by osmotic forces and
support their argument with the statement that sugar and
pectins are present in lesser degree in sour cherries, which
do not crack as badly as sweet cherries. The qualitative
and quantitative differences of these colloids and their
capacity to absorb water is important in the above con-
sideration.

Verner (86, pp. 54-57) believes that calcium in cal-
cium sprays reduces the permeability of plant cells to
water, but does not completely prevent it from absorbing
water. He found calcium hydroxide best as compared to
other calcium salts for this purpose. In his latter trials
(85, pp.271-274), Verner found calcium acetate better than
calcium hydroxide in sprays on the basis of its greater
solubility in water. Gerhard, English and Smith (33,
pp.191-198) are practically of the same opinion as Verner,
Verner and Blodgett (85, 86, 84).

Bullock (18, pp.243-253) found that mineral salts,
whether injected in the form of a solution or inserted dry
into limbs of cherry trees, made no significant difference
in the cracking tendency or composition of the fruit. He
found, however, in his immersion trials that aluminum
sulphate, aluminum chloride, copper sulphate, aluminum
nitrate, calcium hydroxide and calcium acetate, in the
decreasing order reduced the cracking index. He also found
that the cationic effect is more pronounced than the
anionic effect. Of the anions, only the acetate and hy-
droxyl gave noticeable benefit, and of the cations, calcium,
copper, iron, aluminum, thorium and uranium effectively
reduced cracking. Cracking is reduced with the increase
of valence of cations. H^+ ion increases, whereas OH^- ion
decreases the cracking index, although the effect of other
ions usually overrides the pH effect on cracking. He
emphasizes the fact that the range of effective concentra-
tion of these materials is very small. Size of the crop,
temperature and sugar content affect the cracking index.
He believes that these different cations reduce the perme-
ability of the cell membrane by combining with the exposed
carboxyl groups of the pectinous substances; divalent and
trivalent ions by tying two or three molecules and replac-
ing hydrogen as compared to univalent ions. These ions
may even actually block the lenticles and thus reduce the

permeability of the cell membrane. Growth promoting chemicals also reduce permeability. Bullock believes that cracking is thus the result of permeability, osmotic concentrations due to sugars and other substances and the swelling of the colloidal substances like pectin. Sianes (73, p.40) is almost of the same opinion as Bullock (18, pp.243-253) and found cuprosyl sprays best for preventing cherries from cracking. Powers and Bollens (67, pp. 334-335) found 0.1% anyhdrous copper sulphate in solution better than lime-hydrate in preventing the cherries from rain-cracking. Promising results were also obtained by spraying cherries with lime and sulphur together. Borax (Boron) either in solution or when added to soil, prevents cherries from rain-cracking. The residual effect of boron in the soil also prevents cherries from rain-cracking. They also found in their immersion trials that the gain in weight by cherries is due to the absorption of water through the skin and not through the leaves or the stems. Whittenberger and Hills (87, pp.29-31) are of the opinion that by varying degree of bruising, cherries can be made to gain, lose or show no change in weight on immersing in water. This is affected by the temperature and aging or conditioning. Unbruised cherries gain in weight and firmness on soaking but decrease in soluble solids and acids. The main pathway is the tissue exposed by the removal of

stems. The firmness can be increased by lowering the temperature and treating with calcium ion and by conditioning or aging them. Unlike other authors, as given above, they do not believe that the factor of maturity plays an important part in this.

Similar observations regarding the mode or mechanism of permeability through osmotic pressure differences and the ion exchange have been explained by several authors like Stiles and Jorgensen (78, pp.420-434); Osterhaut (63, p.500) and Kabo (42, p.3043). Raber (69, pp.298-308) explains permeability on the basis of electrical condition of the membrane; Krehl and Winters (49, pp.88-89) with their work on rasins and ion exchange, explain it on the basis of valence of ions, and pH changes. Felton (30, p.9) explains it by the magnitude of the charge and the radius of hydrated ions in a solution; Kumin and Myers (50, p.2876) on the basis of structure, valency, ionization constants and the concentrations; Boyd et. al. (16, p.2824) on the basis of valence of ions.

It is important, however, to note here, that there is quite a bit of variation, particularly amongst the groups of the same valence in regard to their effect on the permeability. This is evidently due to the different substances, these various investigators were dealing with, along with different conditions of experimentation and methods of

determination.

Pectic Substances and Their Role in Softening and Cracking of Fruits:

> The pectic substances show almost endless varia-
> tion in properties and behavior. Since the methods
> of definition and characterization are so limited,
> it is not surprising that contradictions are numer-
> ous in the literature concerning their behavior.
> The divergence, however, is more disheartening in
> the interpretation of these observations. This
> is mainly due to the uncrystallized state of our
> knowledge of the structure of the pectic substances,
> which leaves too great a latitude for personal
> interpretation. At times several different types
> of observations are manifestations of the same
> property and are closely interrelated. (47, p.130)

Since the discovery of water-soluble jellying prin-
ciple from plant juices by Vanquelin and Bracannot in 1825,
pectin has attracted considerable attention, but most of
the modern studies on its constitution have been made since
1917. Natural pectins are usually composed of mixtures of
several different types, and of different building stones.
The difficulties of working with these substances, were,
and still are, considerable, as pectin substances form
only a small part of the large number of polysaccharides,
polyuronides, and gums naturally occurring in plants.
(47, pp.1-13; 62, pp.4-5; 41, p.39; 61, p.1).

In regard to maturation studies and its correlation
with pectic constituents, it has been shown by several
workers that most of the deciduous fruits (21, pp.704-712;
20, pp.60-69) soften during ripening period and in storage.
This is associated with the hydrolysis of protopectin, (which

decreases), to soluble pectin, (which increases). Gerhardt
and Ezell (32, pp.62-64; 27, p.9) state that there is a
direct correlation between the loss of ripening capacity
and the inactivity of the hydrolytic system responsible for
the formation of soluble pectin. On overripening or break-
down of fruit, there is more of a change in pectic sub-
stances in the middle lamella instead of those in the cell
wall (15, pp.494-496; 41, pp.40-41). In the former case,
pectin is connected with the cellulose, proteins and other
substances through multivalent cations such as calcium to
form aggregates or through other weak bonds or intermolec-
ular forces. Kizel and Yatsyna, as quoted (41, pp.40-41),
state that pectic substances are formed in the cell itself
and main source of it is cell-sap, though some of the dis-
solved pectic substances may at times originate from insol-
uble pectic constituents of the cell walls and the middle
lamella. Pectic materials in the state of transition can
always be found in plant tissues due to dissolution as a
result of maturity and disintergration of the tissue. Some
botanists have suggested three layers of pectic substances
with varying degrees of combinations with cellulose, hemi-
cellulose, lignin, proteins and other substances and nat-
urally these show different behaviors under different con-
ditions like ripening or storage, or pickling. The thick-
ening of cell wall or dissolution of these layers giving

rise to primary layer or middle lamella and the formation

of calcium and magnesium pectates and pectinates are ex-

plained on these bases. There is a difference of opinions

amongst different workers. Some suggest that middle lamella

is composed entirely of protopectin or of a protein-pectin

complex, whereas others suggest that it is calcium pectate,

which is very similar in nature to protopectin. The role

of protein particularly in regard to rendering soluble

substances insoluble cannot be ignored. When the fruit be-

comes ripe or overripe, decreasing of protopectin in the

primary cell wall which is rich in it and also pectates

(47, pp.544-545; 41, pp.41-42) causes the loosening and

decreased cohesion of the cells and thus softening of the

tissue. This goes on during senescence; the cells become

entirely separated from one another owing to the almost

disappearance of the pectic substance. Other reactions,

still little understood, are also important (47, pp.544-

545). Kertesz (47, pp.278-279) states that middle lamella

is pliable besides being intercellular cement, and gives

the tissues the required firmness, while it is needed, and

is reduced when not required. Some authors have expressed

doubts that pectic substances also play a role in the

water-relations and provide some of the forces necessary

for water movement. It has also been suggested that the

cracking of certain fruits under conditions of plentiful

water supply and rapid growth may be the result of the rapidly increased rate of formation or swelling of colloidal constituents such as pectic substances (43, pp.769-771). Conrad as quoted (47, p.299), found 11.4% pectic substance in an unripe sample of cherries (on the dry matter basis); pectic acid was missing and in the corresponding ripe sample, 4.3% pectic constituents. Lampit and Hughes (51, pp.32-34) give the average pectic content of four samples (stonefree) cherries as 0.35% (0.24-0.54%). This is on fresh weight basis. Money and Christian (53, pp.8-12) on their statistically analyzed data from 1925 to 1948, found in six samples of Morello cherries, an average of 0.16% calcium pectate, while in 15 samples of red and 14 samples of white cherries, the contents were 0.28% and 0.31% respectively.

Several investigators have worked on other fruits like pears, peaches, apples, potatoes, sweetpotatoes, etc., and reported controversial findings in regards to pectic substances and their role in the phenomenan of firming and cracking of fruits.

The changes in ripening or in cold storage has been ascribed to the activity of the naturally occurring pectic enzymes and in some cases to fruit acids, and in still other cases to the transformation of protopectin into pectin and its subsequent degradation products due to the

action of hydrogen peroxide formed by certain dehydro-
genases present in plant tissue. Similar phenomenon was
found in cooking of potatoes, when their tensile strength
decreased (52, pp.499-508). The bulk of the evidence is
definitely in support of the theory that the pectic sub-
stances in the intercellular layers occur as insoluble po-
lygalacturonates, both as calcium pectinates and pectates.
Although calcium is the chief bivalent ion, magnesium may
also be present. The protopectin may remain unaltered in
the cell wall in which it is laid down, or may be changed
to hemicellulose as tissues become older or may be con-
verted to soluble pectins, pectinic acid, or further
hydrolyzed to galacturonic acid with clevages of methyl
alcohol. The nature of the transformation depends upon
the type of the tissue and the conditions of storage. In
fruit tissues, protopectin usually undergoes degradation
to less highly polymerized and methoxylated pectic sub-
stances. The pectinates and pectates in the intercellular
layer also undergo changes during the aging of the cell
wall. The pectic substances decrease, and at the same
time parenchymous cells become loosened or completely
free from one another. All investigators, until recently,
have been in agreement as to the degradation of the pectic
substances in fruits during ripening and cold storage. Of
particular interest, therefore, are the few exceptions like

pears and sweet potatoes in cold storage, where there was development of protopectin instead of its hydrolysis to the degradation substances (27, p.29; 43, p.770; 44, pp.14-15; 41, p.42).

The chemical changes which occur during pickling are manifold and are still little understood (47, p.545; 5, pp.110-112). It seems that one of the important phases of pickling various plant tissues, like cucumbers, is crispness and firmness, which is possible only through the retention of essentially intact cellular structure. The cellular deterioration which causes the "mushy" texture of dill pickles appears to be the result of the partial degradation of insoluble pectic constituents caused by the presence of bacteria which produce pectic enzymes. The softening is caused by the dissolution of the pectic materials in the middle lamella between the cells in the tissue. Kertesz (47, p.547) states that one reason why the role of pectic constituents in such processes as pickling and cooking is not sufficiently clear at the present time is the lack of simple and dependable means of evaluation of degradation processes by means other than or in addition to quantitative determinations; pectic substances may give the same values in a determination of the calcium pectate method for example, but show a wide range of colloidal properties. In case of soluble pectinic acids this degradation can

easily be demonstrated by viscosity changes or gel-forming ability. The situation is vastly more complicated in the case of the ill-defined water-insoluble pectic constituents of plants, for which exact information concerning their structure or even their composition is still lacking. This will continue to be so until better methods are available for evaluation of the changes which may occur in the insoluble-pectic fraction, whether these are rendered soluble in the same process or not. Kertesz (47, p.55) states that protopectin is now believed by some to represent very large (and therefore water-insoluble) pectinic acid molecules. During the solubilization of protopectin, fissure of some of the linkages involving carboxyl group occurs, accounting for the free acid groups found in all water soluble pectinic acids. The existence of polyvalent ions in bonding pectinic acids into protopectin, is only a special case of this sort.

Some Physical and Chemical Properties of Pectic Substances:

Protopectin: Protopectin, while insoluble in water (14, p.402; 41, pp.41-42), is exceedingly susceptible to a long list of reagents and treatments of widely divergent nature, and gives rise to soluble compounds of various characteristics. Its nature is one of the most intricate problems in pectin chemistry. Even the theories of the most modern school of thoughts have the earmarks of working

hypothesis rather than of well substantiated facts. One
reason is the extreme difficulty of separating protopectin
from other water insoluble components without causing de-
gradative changes. Furthermore, the line of division
between protopectin and soluble pectin compounds is arbi-
trary. Controversial claims have been made as regards its
structure and composition and its combination with cellu-
lose and other non pectic substances and the bonds of
forces involved therein. (47, p.72; 41, pp.40-41; 57, p.
38). The insolubility of protopectin in cold water is due
to (1) its association with cellulose proteins, and lignins;
(2) the presence of excessive polyvalent ions; (3) its
large molecular size; (4) combinations of these factors.
(47, pp.75-76; 14, p.418). On hydrolysis with hot water or
even cold acid, protopectin becomes soluble with simulta-
neous removal of the elements mentioned above.

The process of solubilization of protopectin with cold
or hot acid is yet unknown. Some claim that the acid acts
through removal of bivalent cations by hydrolyzing the
cellulose-pectinic acid complex or by simple hydrolysis of
a large and thus water-insoluble molecule. There are
various arguments for and against it (47, p.136). Sabour-
noff and Kalebin (71, pp.275-277, 280, 283) in their series
of experiments, found that sulphurous acid with concentra-
tions up to 0.20% does not produce any precipitable increase

of soluble pectin but over it, it does increase the soluble
pectin in apple pulp stored with SO_2. This increased in
the earlier stages of storage and was up to 30 to 50 % of
total pectin present, but remained constant after it. This
indicates the differentiation between some part of proto-
pectin which has the property of being rapidly hydrolyzed
and another part not, the latter part possessing a far
lower jellying power than the former. Higher SO_2 concentra-
tion results in a decrease of the jellying power of pectin.
Nichols Roy (62, pp.88-90) found that under different
storage conditions, concentrations of SO_2 do not affect
the pectic changes in apricot pulp even with the addition
of 0.05 % $CaCO_3$, but found that 32° F. temperature stor-
age favors greater pectin retention over 90° F. temperature
storage.

Similar is the action of alkalies on protopectin, ex-
cept that it is more drastic and decomposes protopectin,
particularly if alkalies are in higher concentrations.
Complete demehylation of protopectin is caused by alkali
treatment and protopectin finally dissolves in it. The
insoluble portion is cellulose. Calcium and magnesium are
removed like acid. Sometimes hard and difficultly soluble
masses are formed due to these elements (47, p.137).

Protopectin can take up and retain several times its
weight of water, swells up gradually until a maximum degree

of inhibition has occurred. This capacity of retaining water by protopectin is attributed to cellulose which either occurs or is a component of protopectin or by partial hydrolysis of protopectin into pectinic acid. Gaddum (31, p. 20) states that degree of methylation is less in soluble pectins than in protopectin and keeps on declining in the former case, whereas it remains constant in protopectin as the maturity progresses.

Other Pectic Substances: As regards hydrolysis of other pectic substances and its correlation to methoxyl value, there is a great diversity of opinions. Hills et. al. as quoted (61, pp. 32-36) are of the opinion that pectin has methylester groups but no methoxyls. Several workers (79; 40; 31; 61, p. 32) favor the view that the jellying power of pectinic acid decreases with decreasing methoxyl value, whereas Myers and Baker (58, 59, 57, 55, 56) on the other hand concluded that the methoxyl value was no criterion of jellying power, but it was dependent upon the degree of polymerization (molecular weight). This was supported by several other workers as quoted (61, p. 32). Schneider and Bock as quoted (61, p. 32) reported, that methoxyl value often parallels chain length and for this reason may be an indirect index of jelly strength; polygalacturonic acid chain mainly affecting the above, whereas non-galacturonide constituents acting only as diluents.

Temporary exposure to cold dilute acids or even to
their high concentrations does not alter pectinic or pectic
acid., There is a gradual removal of ester groups and over
50°C. the rate is much faster for progressive demethyla-
tion and there is a fissure of 1-4 glycosidic linkages,
This is followed by decarboxylation and further decomposi-
tion of galacturonic acid. Araban fractions are readily
removed as compared to galactans (38; 61, p.47) and is
faster than enzymes in the above removal. Pectic acids be-
have in the similar fashion with the exception of demethyla-
tion. Calcium pectate is much more resistant to the decar-
boxylating action of hot acid than are pectinic acids
(47, pp.136-137). The particle charge is reduced and there
is an increase in tendency of the pectinic acid molecules
for association (47, p.197), whereas, undissociated car-
boxyl groups are capable of jelly formation. Temperature,
pH, and acidity affect this jelly formation in the pH
range of 2.8 to 3.9. Temperature affects it especially be-
low pH of 3.0. Partial and random deesterification as
obtained with acids or bases, produces more valuable
pectinic acids for gel purposes than by enzymic action
(14, p.422). In highly buffered solution, pH has no ef-
fect. Jelly formation is dependent upon total acidity,
pH, concentration of pectin, kinds of salts and their con-
centration and temperature. Removal of methoxyl

groups is considered as the function of hydrogen ion. The jelly formation cannot occur until a certain number of these groups are split off (55, pp.33-34), lower concentration of sulphurous acid or SO_2 (up to 0.30%) does not exert any influence on pectin but at higher concentration, they do, due to pH. (71). Charley and his co-workers (24, pp. 255-263; 23, pp.117-121; 22, pp.362-367; 62, pp.19-21) found that pectin was lost in SO_2 storage of some fruits but greater loss occurred in the cold process than in the hot treatment with SO_2 solution. Morris (54) found similar results and observed that heating the fruit pulp before storage in SO_2 helped to increase the setting power of the fruit as compared to the storage of the raw fruit with SO_2. This increase was not due to increase in pectin content, but was attributed to some alteration in the nature of the pectin.

The action of alkalies is similar to acid. Upon addition of alkalies to a dilute solution of pectinic acid, the free acid groups are engaged in salt formation, giving first acid and then neutral pectinates and as soon as the solution becomes alkaline on further addition of alkali, demethylation occurs with greater velocity and the bulk of ester groups may be removed in a few minutes at room temperature (52, p.507; 47, p.137). Loss of colloidality is clearly observable upon the precipitation of pectic acid or

calcium-pectate from the solutions showing the increased
alkali-consumption. The "secondary" alkali consumption is
dependent upon the temperature and the duration time of
reaction. Strong anhydride and lactone linkages are held
responsible for these low equivalent weights of pectic acid,
which are attacked in an alkaline solution, causing degrada-
tion both in molecular weight as well as colloidal proper-
ties. The formation of such gels is reversible in case of
sodium and potassium hydroxides, but with calcium and bar-
ium hydroxides in similar conditions, these are hard gels,
which do not dissolve in excess of the reagent. This is
due to the different solubility properties of various pec-
tates (47, pp.138-140; 14, p.421). Alkali-deesterification
is retarded by alcohol and accelerated by electrolytes and
is more drastic than acid (61, p.33). Newbold (61, p.34)
in contrast to above, states that pectic acids are not
completely deesterified by the action of alkalies. Action
of enzymes under different condition on the pectic sub-
stances and their nature has been given in an extensive
review by Phaff and Joslyn (65) and others and hence not
given here. These are, however, very important in view of
the fact that acid, alkalies and different electrolytes
under different conditions affect different enzymes in
fruits and thus produce an indirect effect on the firmness
of the tissue.

The hetrogeneity of pectic substances due to the con-
stant transition in fruits or plant tissues during the per-
iod of ripening, is well established. Kertesz states (47,
pp.89-93) that it is unlikely that in any preparation of
pectinic acid all the various polygalacturonic acids would
contain the same proportion of methyoxyl or carboxyl groups
or even the same degree of polymerization. Their arrange-
ment may be regular or irregular and the linkages involved
as well. The pectin molecule, being asymmetrical, increas-
es its heterogeneity. The two samples of pectinic acids
may be identical with regard to molecular size and size
distribution, but the distribution of the methyl-ester
groups within any given molecular size group is different,
even if the average degree of esterification is the same.
Thus, these two samples will show different behavior espec-
ially in acidic properties and reactivity toward polyvalent
ions. The proportion of "ballast" material will further
increase this heterogeneity and their behavior, along with
the effect of temperature, pH, and other factors (61, pp.
1,9,10,66,70; 14, pp.396-411; 47; 41, pp.45-48; 9, pp.3-32;
12, pp.6,16,36; 56; 59, p.36; 89, pp.82-85).

The above factors, along with others like mineral
elements, sugar concentration, solubility behaviors of
pectins, temperature, pH, etc., naturally would affect
viscosity and jellification (47, p.161-164; 61, pp.96-112;

41, p.47).

Firming of Fruits and Vegetables with Calcium Treatment:

Although it has been known for many years that under certain conditions, treatments with calcium has a firming action on many plant tissues, it was not until 1937 that the systematic development of such methods commenced (48, pp.552-553; 45, p.12; 46, p.26). Calcium treatment is now widely used for firming many food products of plant origin and its action is associated with pectic constituents. Calcium chloride-dipping or in the form of a tablet or cal- cium sulfate, calcium citrate and phosphates due to their less hygroscopocity as compared to calcium chloride have been used for canned tomatoes since 1940 to prevent them from disintegration and also to satisfy exacting color requirements. Conrad and Bertsch (25, p.2672) recommended the use of basic calcium chloride (Ca (OH) Cl $\frac{1}{2}$ H$_2$O) due to its easy machine-feeding and less hygroscopocity. The calcium applied in field in the form of sprays does not find its way to the fruit and does not cause a firming effect, when the fruit is canned or processed (47, p.554). As regards the mechanism through which calcium firms the tissue is a matter of controversial nature. (46; 45; 47, p. 555). It is now believed that pectinic acids of ripe fruit form insoluble compounds with calcium and so do the other non-pectic constituents of plant tissues. The possibility

and probability exist of deesterification due to enzymes, acid or alkali treatments and thermal maceration and then its further reaction with calcium salts. Canned fruits seem to react better to calcium firming than do the raw fruits. Similar firming is accompanied by a group of elements, the so called "alkali earth" group (45, p.12; 46, p. 26). Locanti and Kertesz (52, pp.499-508; 47, pp.555-556) claim calcium pectate and calcium pectinate as the material responsible for firmness of the fruit, which are not found in the untreated fruit. Kertesz and McCollach (44, pp.11-12) did not find any significant difference in the amounts of pectic substances in tomatoes of different maturity as judged by color, except a minor difference in degree of esterification. Similarly firming effect was noticed in apples (47, p.556) though varietal and maturity differences were more pronounced. Calcium shows little effect on definitely overripe fruit. The mechanism of this firming reaction in these fruits is not still well established except that there seems to be an unusual agreement among the various investigators that the pectic constituents in fruits and vegetables are responsible for the firming observed upon the treatment with calcium. The total acidity, pH, concentration, and the seasonal variation make a marked difference in the firming reaction of fruits (28, pp.11-12; 39, pp.37-42; 37, p.786). Holgate and Kertesz found a

slight superior firmness of apple slices treated with cal-
cium lactate and the amount of calcium retained by these
apples was more with this treatment than other calcium
salts. They concluded, however, that the effectiveness of
various calcium salts (chloride, phosphate, citrate, malate,
and lactate) in causing a better retention of the firmness
in canned and frozen apples during processing seems to be
comparable when used on equal calcium level basis. Baker
(13, pp.197-198) in explaining the role of calcium salts
in firming of apple slices and other fruits, states, that
the threshold of calcium content required to make calcium
pectate insoluble in water is somewhere around 4.7%. This
is about 50% of the theoretical amount of calcium in cal-
cium pectate (10.20%). He quotes other authors, who found
from 0.15% calcium chloride as the most favorable concentra-
tion and obtained best coagulation results at a level of
about 1% calcium pectate in the pectate gel. Baker further
states that pectic substances exist in fruits and vegeta-
bles as protopectin, pectinic acids, pectinates, pectic
acids and pectates. Analysis is difficult and the exact
proportion of anyone of these substances at any time can
not be predicted. Due to hydrolysis of protopectin by the
action of enzymes or fruit acids, pectinic and pectic acids
are formed. Reaction with available cations takes place
readily as deesterification proceeds and pectinates are

formed. The pectinates consist of a heterogenous mixture of pectin units of varying degree of polymerization and methylation with random cross linkages and interlinkages through available polyvalent cations. Vegetative structures vary with the type of pectinate formed; the sodium and potassium pectinates add little to the structural strength due to being easily soluble, but the pectinates produced with calcium, iron and aluminum add strength in accordance with the degree of esterification of the pectins and they are also insoluble under certain conditions of acidity in plants. As the methoxyl contents of the pectic substances are decreased, their reactivity increases until finally pectic acid or the pectates, salts of pectic acid are formed. In the earlier states of maturity pectic substances are more in the form of protopectin and highly methylated pectinates than are pectins in the ripe fruits. Varietal, soil and climatic differences will introduce variations in the proportions of pectic constituents and consequently their behavior. When insufficient cations are present, the pectinic acids will not have had a chance to react in unripe fruits. Therefore, there are two possible ways in which a calcium salt will aid in firming the tissues of unripe fruit: first by furnishing needed cations for the firming (acid pectinate + calcium chloride →　calcium pectinate + soluble acid chloride): second by

cation exchange of calcium - a firming agent, for sodium -
a non firming agent (sodium pectinate + calcium ⟶ calcium
pectinate + sodium). Baker (13, p.198) states further that
calcium would tend to act as a precipitant for all pectinic
acids judging from above, actually this is not so. The
methoxyl content has to be lowered to about eight percent
before pectinic acids can be precipitated with calcium salts
at pH 4.5. A lower methoxyl value is required at lower pH
values. The actual firming amounts of calcium salt nec-
essary to accomplish this firming will depend on the type
and quantity of natural salts present in the fruit tissue,
the degree of ripeness of fruit, and the action of acids
and enzymes either added or naturally present. Many other
products like raspberry, potatoes, sulphured fruits, canned
peaches, olives, have similarly been treated with calcium
salts for firmness (47, p.554; 28, pp.11-12; 68, pp.478-
488).

In connection with sulfured fruits, Woodroof and Cecil
(91, p.5) used calcium carbonate, monocalcium phosphate,
calcium chloride, calcium sulphate, calcium oxide and cal-
cium hydroxide at 0.02% by weight in SO_2 solution (3% by
weight) as firming agents for strawberries, blackberries,
dewberries, peaches, oranges, pears, and apples at differ-
ent stages of maturity and for various varieties. Simi-
larly thirteen vegetables were tried after blanching. They

found variable results with different vegetables, fruits and
their varieties (91, pp.10-11). Peaches and related fruits
were satisfactorily firmed by .05% of calcium carbonate or
.037% of calcium hydroxide; strawberries, .08% and .06%
respectively.

They further state that in brining cherries, the
alkalizing action of the calcium salts is utilized for
accurate control of pH, so the amounts of firming agents to
be used depend very closely upon the degree of ripeness, the
variety and the degree of bleaching required. They found
1,500 p.p.m. or even as low as 350 p.p.m. of SO_2 sufficient
to inactivate organisms like yeast, mold and acetic acid
forming bacteria.

Wiegand et. al. (88) attributes the pH value of brine
solutions as a factor in preventing cracking of cherries
and the type of alkali used. They claim a pH value of 1.94
to be suitable when calcium liquor is used, but found it
unsuitable when sodium and potassium salts are employed.
The latter require definite higher pH values than is suit-
able for calcium. Varietal and maturity differences have
a bearing upon the optimum pH value. For black cherries it
was 1.83. Cracking of cherries in brine has been attri-
buted by them to be due to permeability and osmotic pres-
sure. Cruess (26, p.280) is of the opinion that calcium
ion is not the cracking preventive factor, but cracking is

rather due to high acidity, that is too low pH value. The
critical pH, below which severe cracking occurs after six
months of storage appears to be below 3.1 and 3.3; none at
3.5. Taken on fresh solutions, the critical pH appeared to
lie between 2.25 and 3.0 for calcium sulfate and acid. He
further states that calcium and aluminum either separately
or together in brine firm the cherries as they do in figs,
peaches, olives and vegetables and probably reacting with
pectinious substances. Bullis and Wiegand (17, pp.5-19)
besides the factor of maturity and handling of cherries,
attribute cracking and softening to alkali-acid ratios,
kind of alkali used and the hardening agent employed.
Their observations are in contrast with those of Cruess
(26) where alum either alone or in combination with lime
in brine gave cracked and soft mushy cherries. They found
calcium carbonate superior to lime in SO_2 solution and in
calcium sulfite solution. When lime in calcium sulfite was
used, they got bacterial spoilage. They got very poor
cherries in color as well as cracked and soft when tannic
and citric acids were used, though the former with $CaCO_3$
gave excellent results. Magnesium sulfate alone and in
combination with calcium sulfate gave fair but variable
results. They have emphasized the importance on the stage
of maturity, turgidity of the fruit and weather conditions
when it is picked for brining purposes. They have also

taken into account the bacterial spoilage due to insufficient SO_2 or more lime in the brine as the cause of softening or gas pockets in cherries.

Wiegand et. al. (88, pp.93-100) state on the basis of commercial observations that concentrated sugars, starches and gums pass out through the membrane (here referred to skin) and there is a loss of from 12 to 15 % in weight indicating that the cell constituents do actually pass out through the membrane and role of calcium and magnesium is to decrease this tendency of absorbing water or solution and thus make cherries firm and protect them against cracking. However, excess of lime also produces violent cracking in cherries.

Atkinson and Strachan (4, pp.72-74) state that cherries for processing in SO_2 solution are picked while slightly immature. Napoleon (Royal Ann) cherries are harvested with a total soluble solid content of 15 to 17 %. This and the dark varieties are judged by color as well. The latter should be of a light tomato color. They have assumed that the calcium combines with pectin in the cell walls to form insoluble calcium pectate, and thus prevents the collapse of the fruit. They further state that, so long as the content of the elemental calcium in the formula is the same, different kinds of calcium compounds are comparable in hardening or firming of the tissue. They found

English bolted whiting ($CaCO_3$) very satisfactory. They
(4, p.73) further suggest to store cherries for about 12
hours, if they are free of rots and splits before barrel-
ing. Though it is not necessary, it is of assistance in
reducing the number of split cherries. Theoretically the
fruit loses some of its firmness through loss of moisture
and thus may absorb a small amount of preservative solution
without developing an abnormally high pressure.

Atkinson and Strachen's work (6, p.142) is mostly on
the effect of acid-alkali ratios on the color of the brine
and its correlation to softness and cracking of cherries.
The pH of the solution as well as cherries at the most
colorless stage was in the neighborhood of 5.0 to 5.5 as
determined colorimetrically. Fruit and solution, when
treated with calcium chloride, turned bright red. The
flesh was soft and cracked. Sodium hydroxide had a ten-
ency to lessen the pink color and soften the tissue. Vary-
ing amounts of calcium carbonate tend to firm the fruit,
reduce the cracking to a minimum and lighten the pinkish
color. Sulphuric acid caused the fruit and the liquid to
become red, but the firmness was not markedly changed.
Fruit treated with sulphurous acid without addition of
calcium became very soft, red in color and badly cracked.
With sodium chloride, the fruit was soft. As regards the
effect of pH on firmness of cherry tissue, they state

(6, p.142) that calcium carbonate and calcium hydroxide caused improvement namely firmer flesh, less pink color and minimum cracking. The softening of the flesh was not prevented with the other calcium compounds used when a strong acid ion such as chlorine was in the salt. Their results showed that one percent sulphurous acid solution containing sufficient calcium compound to give a pH of 2.0, yields the most satisfactory results. They further state that besides the effect of pH, there is also a definite variety and maturity effect on the number of perfect cherries. This is in harmony with Wiegand et. al. (88, pp.93-100) who reported the optimum pH value of brine for Royal Ann cherries to be 1.94 and for dark varieties, 1.83. Atkinson and Strachan (6, p.142) tried further experiments on maturity of different varieties of cherries and its correlation to the color of brine and fruit and found from 11.8 to 17.0% soluble-solids-cherries suitable for brining whereas over 18%, the color of brine was strong pink.

Ross (70, pp.40-42) states that low temperature appears to be a factor in the skin-cracking, whereas the direct effect of elevated storage temperatures is to hasten firming and accelerate bleaching in brined cherries, however, high storage temperature may cause softening indirectly by promoting an excessive loss of SO_2. This is in contradiction with Bullis and Wiegand's recommendations

(17, p.8) of storing the barrels of brined cherries in cold
storage rooms like basements protected from the heat.
Atkinson and Strachan (4, p.72-74) are in harmony with
Bullis and Wiegand's (17) recommendations of storing brined
cherries in cool places and not expose it to direct sun-
light.

CHAPTER III

METHODS AND MATERIALS

Source, Harvesting and Handling of Royal Ann Cherries:

About 150 pounds of Royal Ann cherries were procured

through the generosity of the Willamette Cherry Growers

and Briners Association, Salem, Oregon, in the middle of

July, 1950. About the same quantity of the fruit was

picked by the author from two trees in Corvallis. These

were thoroughly mixed for getting a uniform and representa-

tive sample for experimental work. The previous history of

these trees was not available as regards irrigation and

addition of fertilizers, with the exception that these

trees were not sprayed with any chemicals during the season.

During the time of experimentation, these cherries

were kept in a cold storage at 40° F. Before packing them

in glass quart jars, these were sorted free of rotten, rain-

split or bird-pecked cherries.

Maturity: Maturity of the fruit at the time of harvesting

was judged by the color. Although it was fairly late in

the season when the cherries were picked from the trees,

the sample was considered representative for the whole

season as it contained from very ripe to not fully ripe

cherries. The representative sample of this lot was also

analyzed for soluble solids by hand refractometer and total

solids by the official method, as will be given later.

Experimentation: The method in commercial use, as given by
Wiegand et. al. (88, p.94) was followed but on the corre-
sponding miniature scale and in glass jars instead of
wooden barrels. The commercial method as followed in the
Northwest consists of filling standard 50 gallon paraffin-
lined, fir barrels with from 240 to 250 pounds of fresh
cherries, covering these cherries with brine and storing
with some agitation until they are ready to be pitted and
stemmed.

In duplicating the above procedure, 250 pounds of
cherries and about 200 pounds of brine were considered
standard for the experimental work.

Brine: Brine consisted of 1.25% of SO_2 solution made by
bubbling compressed SO_2 into distilled water. The strength
of the sulphur dioxide solution was checked by the method
followed by Bullis and Wiegand (17, pp.5-7) and is the
same as official standard iodine titration method (1, pp.
80-81).

Hardening Agents in the Brine: Keeping CaO as standard and
at the rate of 5 pounds per 100 gallons as is generally
used commercially in barrels, the following is the table of
the different chemicals used with the quantities calculated
at same calcium levels as is in calcium oxide and made up to
two liters with the sulphur dioxide solution as given above.

The resultant solution is called brine. This is one set of
brines at their natural pH. Similarly, another set of such
brines was made, but their pH was controlled at 3.0 by the
addition of either concentrated sodium hydroxide or concen-
trated hydrochloric acid.

Table 1

Different Chemicals Used as Hardening Agents

Name of the chemicals	Weight in grams per 2 liters of brine	Natural pH	Remarks
Calcium oxide (CaO)	12.05	2.40	Soluble
Calcium lactate ($Ca(C_3H_5O_3)_2.5H_2O$)	66.23	2.80	Soluble
Calcium chloride ($CaCl_2$)	23.84	1.34	Soluble
Calcium citrate ($Ca_3(C_6H_5O_7)_2.4H_2O$	40.85	2.68	Very slowly soluble
Calcium orthophosphate (dibasic)($CaHPO_4.2H_2O$)	36.98	2.52	Soluble
Magnesium oxide (MgO)	14.27	6.34	Less soluble. Yellow solution
Magnesium chloride ($MgCl_2.6H_2O$)	71.98	1.30	Soluble
Aluminum potassium sulphate ($Al_2(SO_4)_3 K_2SO_4.24H_2O)_2$	151.45	1.68	A saturated solution
Thorium nitrate ($Th (NO_3)_4.4H_2O$)	20.48	1.36	Not soluble. Tends to precipitate
Uranyl nitrate ($UO_2(NO_3)_2.6H_2O$	18.16	1.48	Less soluble. Yellow solution.
Sulphur dioxide solution 1.25%		1.62	

The pH of fresh cherries was 3.88

<u>Treatments:</u> Quadruplicate one-quart glass jars for each treatment were filled with one pound each of the cherries and were covered with the respective brines and the glass lids tightly screwed down to protect against evaporation and spoilage. They were labelled giving description of the treatments, pH, temperature of storage and the date of packing. In short, each kind of brine, as for example, calcium oxide brine at its natural pH, was used to fill four quarts of cherries. Similarly, calcium oxide brine controlled at pH 3.0, was used to fill other four quarts of cherries. Two quarts of the former treatment and two quarts of the latter treatment were placed for storage at room temperature, (70° F., range 68°-72° F.) and another set in cold storage (40° F., range 38°-42° F.) for a period of about one year. In this way, it was planned to observe the effect on the cherries of each brine under its natural pH and also at controlled pH of 3.0 under two different temperature conditions of storage. The treatments are shown in table 2.

TABLE 2

Treatments of Cherries with Different Brines
At Its Natural and Controlled pH Under Two Temperatures
Storage Conditions

Serial no. of treatments	Treatment	Room temperature (68°-74° F)		Cold Storage (38°-42° F)	
		Natural pH	Controlled pH	Natural pH	Controlled pH
1.	Calcium oxide 2.4		3.0	2.4	3.0
2.	Calcium lactate 2.80		3.0	2.80	3.0
3.	Calcium chloride 1.34		3.0	1.34	3.0
4.	Calcium citrate 2.68		3.0	2.68	3.0
5.	Calcium orthophosphate 2.52		3.0	2.52	3.0
6.	Magnesium oxide 6.34		3.0	6.34	3.0
7.	Magnesium chloride 1.30		3.0	1.30	3.0
8.	Aluminum potassium sulfate 1.68		3.0	1.68	3.0
9.	Thorium nitrate 1.36		3.0	1.36	3.0
10.	Uranium nitrate 1.48		3.0	1.48	3.0
11.	Sulphur dioxide solution 1.62		3.0	1.62	3.0

Thus there were eleven treatments with two variables of pH which in turn had two more variables of the storage temperature conditions. After about one year's storage period, the cherries were tested for free and total SO_2 in the brine, final pH, firmness, brine cracks (checks or splits), color of the cherries and the brine, soluble solids by a hand refractometer, total solids by weight, alcohol-insoluble solids, protopectin, soluble and total pectin and the amounts of the mineral elements in the cherries. The following methods were used:

Free Sulphur Dioxide: See page 36 in paragraph entitled "Brine".

Total Sulphur Dioxide: This method is essentially the same as the official A.O.A.C. method (1, p.81) with certain modifications.

Ten milliliters of the brine sample were pipetted into a 125 milliliter erlenmeyer flask containing 50 milliliters of distilled water. Then 5 milliliters of 5N NaOH were added and it was allowed to stand exactly 15 minutes. After this, 7 milliliters of 5 N hydrochloric acid were added and it was titrated against a standardized 0.1N iodine solution with starch solution as an indicator and the amount of total SO_2 calculated.

pH: pH values were determined by Beckman pH meter model G, using a glass electrode.

Firmness: The "Universal Penetrometer" with a 50 gram weight was used for measuring the firmness of cherries. A nail with a circular head 3 millimeter in diameter was substituted for the regular plunger. Contact was made at the central convex portion of the cherry. Fifteen seconds were allowed for the penetration. Five cherries were removed at random from a quart jar representing each treatment. This was repeated five times in the random fashion for the above test. Considerable variation was found among the cherries of the same sample.

Brine Checks (cracks): Twenty-five cherries from each treatment were carefully observed for brine cracks or checks externally and internally, the latter being visible when cherry is held against the light. These cracks were measured with a scale graduated in inches.

Color: Visual observations of the color of cherries were recorded.

After these observations, cherries from one quart of each treatment were removed and washed with 1500 milliliters of distilled water on a sieve to remove all the salt adhering to cherries. These were then dried with a towel and frozen immediately in a cellophane bag contained in a cardboard box at -10° C. to arrest any chemical and enzymatic changes which would interfere with further analysis such as hydrolysis of pectic substances, etc.

These were kept in storage at -20° C. till further analytical work. The number of treatments was so great that only samples at room temperature were analyzed for the following after noticing the difference in firmness and brine-cracks as a result of temperature variations.

Two samples at a time were taken out of cold storage and brought to room temperature. The cherries were pitted, the weights of the cherries with and without pits noted, and the number of cherries counted. The cherries after pitting were crushed and made into a pulpy paste in a Waring blendor to get uniform samples for the following tests:

Soluble Solids: Soluble solids were determined by means of a hand refractometer in the crushed samples as well as in their respective brines.

Total Solids or Moisture Analysis: The official A.O.A.C. method (1, p.382) was followed.

Pectic Substances:

Some preliminary trials with fresh cherries were made by Storto's method (80, p.4849), which is a modified form of Carre and Haynes method, but is much faster and easier than most methods employed and may be used with advantage with fair to good accuracy depending upon the product used, in the industries, where a quick determination of pectic substances will be so helpful. This method, however, was discarded as the complete details concerning it were not

available at. that time. Substances, like starch, cellulose, etc., which have similar properties and molecular weights as pectin are likely to interfere. This method gave higher results than the method followed later. It did not serve the purpose of determination of the two constituents in the pectic substances namely protopectin and soluble pectin. The method gives only soluble pectin in a sense as other substances interfere in its accurate determination.

Date's methods (27, pp.22-24) were employed for the determination of alcohol-insoluble material, pectin and protopectin. These methods are slight modifications of the methods employed by Baier (7, p.13); or those employed by Sinclair and Crandall (76, pp.154-160) and Sinclair and Crandall (74, pp.107-108; 75, pp.681-683), which in turn are the modifications of the original Carre and Haynes calcium pectate method (20, pp.60-69).

Mineral Elements:

Cherries, which were treated with calcium, magnesium, and aluminum salts and also the fresh cherries, were analyzed for these elements respectively. Thorium and uranium in the cherries treated with the brines of these salts were not analyzed as satisfactory results were not possible as these salts were firmly coated on the skin and the flesh of the cherries. In spite of the removal of these externally but firmly attached salts to the fruit, by

scraping, the possibility of the error for correct estimation was too great. Satisfactory firming and prevention from brine-cracking was not obtained by these salts in the concentrations used. Furthermore, they are not feasible for commercial use because of their rarity, cost, and probable toxicity. They were used primarily for the basic study of elements of higher valency as given in the Hofmeister series.

Calcium:

Preliminary trials with the fresh cherries using the method given by Tyner (82, pp.76-80) with slight modifications, compared favorably with the official A.O.A.C. method (1, p.388) and was used for all the other treatments as it is easy and rapid to run. The modifications were, that instead of using calcium chloride dehydrate, reagent grade, as standard solution as suggested by Tyner, calcium carbonate (C.P.) in normal hydrochloric acid was used to eliminate the possibility of the error due to the variations in moisture content of calcium chloride dehydrate. There were some more modifications inherent to this problem, also made. Due to the advantages with respect to no interference of pH or other mineral elements, this method was found satisfactory.

Magnesium:

Preliminary trials following Sterges and MacIntire's

method (77, pp.351-353) with some modifications inherent to this problem compared favorably with the official A.O.A.C. method (1, pp.388-389) and it was used for all the magnesium determinations in the samples. It is easy and rapid to run and the presence of other elements does not interfere with its accurate estimation.

Aluminum:

Sandell's method (72, pp.114-119) for aluminum determination with some modifications pertinent to the problem was followed. It is easy and rapid to run and the presence of other elements does not interfere with its accurate estimation. It compares very favorably with the official A.O.A.C. method (1, pp.118-119) as was found from the preliminary trials.

CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

Maturity:

The factor of maturity was common in all the treatments. In spite of the thorough mixing of cherries from three different sources, the possibility and probability of some variation among these samples could not entirely be eliminated due to heterogeneity in maturity of cherries, even though picked from the same tree and on the same day. The total and soluble solids of fresh cherries were 19.0%, and 17.5% respectively. (Table 11, appendix). Cherries in general were at that stage of maturity, when they are more subject to cracking and softening in the brines as pointed out by some investigators (17, p.5; 6, p.142).

Factors Affecting Firmness:

Statistical analysis shows the following factors affecting the firmness of cherries. The role of individual factors will be discussed in details later. From the ranges given in tables 7 and 8 (appendix), it is clear that there is quite a variability in firmness as shown by pressure test readings not only between various chemical treatments, but also in the same treatment under varying conditions of pH and storage temperatures. The order of

ratings of the treatments including all the above vari-
ables is given in table 3.

TABLE 3

Rating of Treatments in Declining Order of Firmness of Brined Cherries as Judged by Universal Penetrometer Pressure Readings and Their Relative Cracking per 25 Cherries

Order of Rating	Treatments	No. of cracks per 25 (Int.&Ext.)	PENETROMETER PRESSURE READINGS			
			Natural pH		Controlled pH of 3.0	
			Room temp. storage (70°F)	Cold storage (40°F)	Room temp. storage (70°F)	Cold storage (40°F)
1.	Aluminum-potassium-sulfate	5			8.08	
2.	Calcium-citrate	3			9.32	
3.	Calcium-orthophosphate	0			9.48	
4.	Calcium-orthophosphate	1				9.68
5.	Calcium-lactate	2			10.24	
6.	Calcium-oxide	8				10.52
7.	Calcium-oxide	11		10.80		
8.	Aluminum-potassium-sulfate	0				10.92
9.	Calcium citrate	3	10.96			
10.	Calcium orthophosphate	2		11.20		
11.	Calcium lactate	2	11.48			
12.	Calcium orthosphosphate	0	11.52			
13.	Calcium oxide	8	11.96			
14.	Thorium nitrate	12				12.12
15.	Calcium citrate	2				12.92
16.	Calcium lactate	6				13.04
17.	Calcium chloride	0			13.28	
18.	Magnesium oxide	9	13.32			

TABLE 3(cont.)

Order of Rating	Treatments	No. of cracks per 25 (Int.&Ext.)	PENETROMETER PRESSURE READINGS			
			Natural pH		Controlled pH of 3.0	
			Room temp. storage (70°F)	Cold storage (40°F)	Room temp. storage (70°F)	Cold storage (40°F)
19.	Calcium lactate	5		13.60		
20.	Calcium chloride	5				13.64
21.	Calcium citrate	3		14.36		
22.	Calcium oxide	1			14.40	
23.	Thorium nitrate	4		15.40		
24.	Aluminum-potassium-sulfate	12	15.68			
25.	Magnesium oxide	2			16.24	
26.	Uranium nitrate	22		18.76		
27.	Aluminum-potassium-sulfate	8		19.36		
28.	Uranium nitrate	7			19.84	
29.	Magnesium chloride	4			20.04	
30.	Uranium nitrate	12				20.08
31.	Magnesium chloride	0				20.32
32.	Thorium nitrate	12			20.56	
33.	Magnesium oxide	12		20.60		
33.	Magnesium oxide	4				20.60
34.	Thorium nitrate	7	20.76			
35.	Calcium chloride	18		20.84		
36.	Sulphur dioxide only	17		21.56		
37.	Uranium nitrate	24	22.96			
38.	Sulphur dioxide only	0			23.44	
39.	Sulphur dioxide only	5				25.72
40.	Sulphur dioxide only	20	26.48			
41.	Calcium chloride	25	29.16			
42.	Magnesium chloride	24	30.32			
43.	Magnesium chloride	23		32.04		

Statistical analysis shows that the firmness of the cherry tissue is mainly dependent upon brine treatments, and pH, but not on the temperature of storage. It is also affected significantly by the first and second order interactions of treatment x pH, treatment x temperature, treatment x temperature x pH, but not by pH x temperature as would be clear from the statistical analysis in tables 4 to 4(e). Significant differences at the 5% level are given in the respective tables for the above interactions.

TABLE 4

Analysis of Variance for Firmness
(Penetrometer Pressure Readings)
In Differently Treated Brined Cherries.

Variation due to	Sum of Squares	Degrees of freedom	Mean Square	F
Replication	21.2535	4	5.3134	1.054
pH	582.5636	1	582.5636	5.425 *
Temperature	0.2626	1	0.2626	0.00392
Treatment	5,673.0611	10	567.3061	8.470 *
pH x Temperature	21.2662	1	21.2662	1.123
Treatment x pH	1,073.8604	10	107.3860	5.670 *
Treatment x temperature	669.7374	10	66.9737	3.536 *
Treatment x temperature x pH	189.3818	10	18.9382	3.76 *
Error	866.4105	172	5.0373	----
Total	9,097.7971	219	------	----

* Significant at 5% level.

TABLE 4(a)

Summary of Means of Treatments
in Regard to Descending Order of Firmness
(Penetrometer Pressure Readings)*
of Brined Cherries.

Rank	Treatments	Means of Pressure Readings
1.	Calcium orthophosphate	10.47
2.	Calcium oxide	11.18
3.	Calcium citrate	11.89
4.	Calcium lactate	12.09
5.	Aluminum potassium sulphate	13.51
6.	Thorium nitrate	17.21
7.	Magnesium oxide	17.69
8.	Calcium chloride	19.23
9.	Uranium nitrate	20.41
10.	Sulphur dioxide only	24.3
11.	Magnesium chloride	25.69

* Least significant difference at 5% level = 5.76

TABLE 4(b)

Summary of Means of pH
in Regard to Firmness
(Penetrometer Pressure Readings*)
of Brined Cherries

pH	Means of Pressure Readings
Natural pH	18.32
Controlled pH of 3.0	15.07

* Least significant difference at 5% level = 3.11.

TABLE 4(c)

Summary of Means of Treatment Combinations (Treatment x Temperature x pH) in Regard to Firmness (Penetrometer Pressure Readings[*]) of Brined-Cherries.

Serial no.	Treatments	Natural pH		Controlled pH	
		Room temp. (70° F)	Cold storage (40° F)	Room temp. (70° F)	Cold storage (40° F)
1.	Sulphur dioxide only	26.48	21.56	23.44	25.72
2.	Calcium oxide	11.96	10.80	14.40	10.52
3.	Calcium chloride	29.16	20.84	13.28	13.64
4.	Calcium lactate9	11.48	13.60	10.24	13.04
5.	Calcium citrate	10.96	14.36	9.32	12.92
6.	Calcium orthophosphate	11.52	11.20	9.48	9.68
7.	Magnesium oxide	13.32	20.60	16.24	20.60
8.	Magnesium chloride	30.32	32.04	20.04	20.32
9.	Aluminum potassium sulphate	15.68	19.36	8.08	10.92
10.	Thorium nitrate	20.76	15.40	20.56	12.12
11.	Uranium nitrate	22.96	18.76	19.84	20.08

[*] Least significant difference at 5% level = 2.80.

TABLE 4(d)

Summary of Means of Treatment x Temperature Groups
in Regard to Descending Order of Firmness
(Penetrometer Pressure Readings*) of Brined Cherries.

Rank	Treatments	Pressure Readings
1.	Calcium citrate (Room temperature)	10.14
2.	Calcium orthophosphate (Cold storage)	10.44
3.	Calcium orthophosphate (Room temperature	10.50
4.	Calcium oxide (Cold storage)	10.66
5.	Calcium lactate (Room temperature)	10.86
6.	Calcium oxide (Room temperature)	11.70
7.	Aluminum potassium sulphate (Room temperature)	11.88
8.	Calcium lactate (Cold storage)	13.32
9.	Calcium citrate (Cold storage)	13.64
10.	Thorium nitrate (Cold storage)	13.76
11.	Magnesium oxide (Room temperature)	14.78
12.	Aluminum potassium sulphate (Cold storage)	15.14
13.	Calcium chloride (Cold storage)	17.24
14.	Uranium nitrate (Cold storage)	19.42
15.	Magnesium oxide (Cold storage)	20.60
16.	Thorium nitrate (Room temperature)	20.66
17.	Calcium chloride (Room temperature)	21.22
18.	Uranium nitrate (Room temperature)	21.40

TABLE 4(d) - cont.

Rank	Treatments	Pressure Readings
19.	Sulphur dioxide only (Cold storage)	23.64
20.	Sulphur dioxide only (Room temperature)	24.96
21.	Magnesium chloride (Room temperature)-	25.18
22.	Magnesium chloride (Cold storage)	26.18

* Least significant difference at 5% level $\simeq$ 4.34

TABLE 4(e)

Summary of Means of Treatment x pH Groups
in Regard to Descending Order of Firmness
(Penetrometer Pressure Readings*) of Brined Cherries.

Rank	Treatments	Pressure Readings
1.	Aluminum potassium sulphate (Controlled pH)	9.50
2.	Calcium orthophosphate (Controlled pH)	9.58
3.	Calcium oxide (Controlled pH)	10.98
4.	Calcium citrate (Controlled pH)	11.12
5.	Calcium orthophosphate (Natural pH)	11.36
6.	Calcium oxide (Natural pH)	11.38
7.	Calcium lactate (Controlled pH)	11.64
8.	Calcium lactate (Natural pH)	12.54
9.	Calcium citrate (Natural pH)	12.66
10.	Calcium chloride (Controlled pH)	13.46
11.	Thorium nitrate (Controlled pH)	16.34
12.	Magnesium oxide (Natural pH)	16.96
13.	Aluminum potassium sulphate (Natural pH)	17.52
14.	Thorium nitrate (Natural pH)	18.08
15.	Magnesium oxide (Controlled pH)	18.42
16.	Uranium nitrate (Controlled pH)	19.96
17.	Magnesium chloride (Controlled pH)	20.18
18.	Uranium nitrate (Natural pH)	20.86
19.	Sulphur dioxide only (Natural pH)	24.02

TABLE 4(e) - cont.

Rank	Treatments	Pressure Readings
20.	Sulphur dioxide only (Controlled pH)	24,58
21.	Calcium chloride (Natural pH)	25,00
22.	Magnesium chloride (Natural pH)	31,18

* Least significant difference at 5% $\doteq$ 4,34

Judging from 4(a), it is quite evident that there is
no particular treatment after excluding other interactions
which could be called the best. The treatment, namely;
calcium orthophosphate, calcium oxide, calcium citrate,
calcium lactate, and aluminum potassium sulfate are statis-
tically in one group, followed by thorium nitrate, magne-
sium oxide, calcium chloride and uranium nitrate in the
second group. Sulphur dioxide only and magnesium chloride
fall in the third group. As regards their ratings, they
are arranged in the descending order as given above. If
these salts were to be arranged in this order in the form
of cations and anions, it would be seen that they do not
follow the same rule or the pattern as given for lyotropic
or Hofmeister series (34, pp.218-222), but are in fair
agreement with Raber's observations (69, pp.299-306).
Raber explains this on the basis of the electrical con-
dition of the membrane and the effects of positive and
negative cations and anions and as affected by the pre-
sence of other interfering ions like chlorides or OH^- or
H^+ and temperature conditions. Judging from table 4(b),
it is evident that the controlled pH of 3.0 gave signifi-
cantly better results than the natural pH as an over all
picture for all the treatments and the two temperatures of
storage. It does not, however, show individual differences
or variations between each treatment, as can be seen from

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tables 7, 8 (appendix), 3, and 4(c).

From table 4(c), which gives the second order inter-
action of all the treatment combinations, it is evident
that different salts under different conditions of pH
and temperatures of storage gave variable results. The
order of ratings for these is given in table 3. Similarly,
table 4(d) gives the first order interaction of treatment
x temperature. As an over all effect for all the treat-
ments together, temperatures of storage do not signifi-
cantly affect the firmness of cherries but when the reac-
tion of treatments and temperature is taken for the indiv-
idual treatments, it does make a significant difference.
The exceptions to the above are clear from the table.
Similarly, table 4(c) shows that besides the effect of pH
alone, which gives a significant difference, the inter-
action of treatment x pH also affects the firmness of the
brined cherries.

Factors Affecting Brine Cracking:

Factors which affect brine-cracking of cherries are
not the same as those which affect the firmness of cherries.
The following are the factors which are based on the sta-
tistical analysis mainly. The individual effects of the
different variables will be discussed later.

TABLE 5

Analysis of Variance for Brine-Cracks in Cherries
(Number of Cracked Cherries for Each 25 Cherries Observed*)
in Differently Treated Brined-Cherries.

Variation due to	Sum of squares	Degrees of freedom	Mean square	F	
pH	633.84	1	633.84	7.845	*
Temperature	2.75	1	2.75	0.473	
Treatment	879.55	10	87.955	1.089	
pH x temperature	16.57	1	16.57	2.848	
Treatment x pH	807.91	10	80.791	13.886	*
Treatment x temperature	76.00	10	7.600	1.306	
Error	58.18	10	5.818	-----	
Total	274.80	43	57.5535	-----	

* Significant

TABLE 5(a)

Summary of Means of pH
in Regard to Cracking of Brined Cherries
(Number of Brine-Cracked Cherries for Each 25 Observed*)

pH	Means of brine-cracks *
Natural pH	11.72
Controlled pH of 3.0	4.13

* Least significant difference at 5% level = 6.04.

TABLE 5(b)

Summary of Means of Treatment x pH Groups
in Regard to Descending Order of Cracking of Brined Cherries
(Number of Brine-Cracked Cherries for Each 25 Cherries
Observed*)

Rank	Treatments	No. of brine-cracked cherries
1.	Calcium orthophosphate (Controlled pH)	0.5
2.	Calcium orthophosphate (Natural pH)	1.0
3.	Magnesium chloride (Controlled pH)	2.0
4.	Aluminum potassium sulphate (Controlled pH)	2.5
4.	Calcium citrate (Natural pH)	2.5
4.	Calcium citrate (Controlled pH)	2.5
4.	Calcium chloride (Controlled pH)	2.5
4.	Sulphur dioxide only (Controlled pH)	2.5
5.	Magnesium oxide (Controlled pH)	3.0
6.	Calcium lactate (Natural pH)	3.5
7.	Calcium lactate (Controlled pH)	4.0
8.	Calcium oxide (Controlled pH)	4.5
9.	Thorium nitrate (Natural pH)	5.5
10.	Uranium nitrate (Controlled pH)	9.5
10.	Calcium oxide (Natural pH)	9.5
11.	Aluminum potassium sulphate (Natural pH)	10.0
12.	Magnesium oxide (Natural pH)	10.5
13.	Thorium nitrate (Controlled pH)	12.0

TABLE 5(b) - cont.

Rank	Treatments	No. of brine-cracked cherries
14.	Sulphur dioxide only (Natural pH)	18.5
15.	Calcium chloride (Natural pH)	21.5
16.	Uranium nitrate (Natural pH)	23.0
17.	Magnesium chloride (Natural pH)	23.5

* Least significant difference at 5% level = 5.47

The analysis of variance as given in table 5 shows
that brine-cracking in cherries is affected mainly by the
pH irrespective of the kind of treatments or the tempera-
ture of storage. It is also affected by the first order
interaction of treatment x pH. Table 5(a) shows that, as
an over-all effect for all the treatments under the two
temperatures of storage, the controlled pH of 3.0 gave
significantly better results than the natural pH at 5% lev-
el. Exceptions to this are clear from the table. Table
5(b) shows the first order interaction of treatments x pH.
Besides an over-all effect, this also shows the indivi-
dual differences between the treatments under the vari-
ables of natural and controlled pH. It should, however,
not be inferred from the foregoing statements that treat-
ment, or temperature by themselves do not play a role in
the cracking of brined cherries. These individual differ-
ences are clearly explained in table 6, which gives the
order of rating for different treatments under different
conditions of pH and storage temperature.

TABLE 6

Rating of Treatments with Regard to Brine-cracking of Cherries in Different Brines, as Judged by Total Number of Brine-cracks (External Internal)

Order of rating	Treatments	Natural pH						Controlled pH of 3.0					
		Room temp.			Cold storage			Room temp.			Cold storage		
		Total no.	Ext.	Int.	Total no.	Ext.	Int.	Total no.	Ext.	Int.	Total no.	Ext.	Int.
1.	Calcium orthophosphate							0	0	0			
1.	Aluminum potassium sulphate										0	0	0
1.	Calcium orthophosphate	0	0	0									
1.	Calcium chloride							0	0	0			
1.	Magnesium chloride										0	0	0
1.	Sulphur dioxide							0	0	0			
2.	Calcium orthophosphate										1	0	1
2.	Calcium oxide							1	0	1			
3.	Calcium lactate							2	0	2			
3.	Calcium orthophosphate				2	0	2						
3.	Calcium lactate	2	2	0									

TABLE 6 (cont.)

Order of rating	Treatments	Natural pH Room temp. Total no.	Ext.	Int.	Cold storage Total no.	Ext.	Int.	Controlled pH of 3.0 Room temp. Total no.	Ext.	Int.	Cold storage Total no.	Ext.	Int.
3.	Calcium citrate										2	1	1
3.	Magnesium oxide							2	0	2			
3.	Calcium citrate							3	0	3			
4.	Calcium citrate	2	0	2									
4.	Calcium citrate				3	0	3						
5.	Thorium nitrate				4	4	0						
5.	Magnesium chloride							4	0	4			
5.	Magnesium oxide										4	1	3
6.	Aluminum potassium sulphate							5	0	5			
6.	Calcium lactate				5	0	5						
6.	Calcium chloride										5	0	5
6.	Sulphur dioxide										5	4	1
7.	Calcium lactate										6	0	6
8.	Uranium nitrate							7	0	7			
8.	Thorium nitrate	7	7	0									
9.	Calcium oxide										8	0	8
9.	Calcium oxide	8	0	8									
9.	Aluminum potassium sulphate				8	8	0						
10.	Magnesium oxide	9	4	5									
11.	Calcium oxide				11	3	8						
12.	Thorium nitrate										12	12	0
12.	Uranium nitrate										12	2	10

TABLE 6 (cont.)

Order of rating	Treatments	Natural pH						Controlled pH of 3.0					
		Room temp.			Cold storage			Room temp.			Cold storage		
		Total no.	Ext.	Int.	Total no.	Ext.	Int.	Total no.	Ext.	Int.	Total no.	Ext.	Int.
12.	Thorium nitrate							12	6	6			
12.	Magnesium oxide				12	12	0						
12.	Aluminum potassium sulphate	12	12	0									
13.	Sulphur dioxide				17	17	0						
14.	Calcium chloride				18	18	0						
15.	Sulphur dioxide	20	20	0									
16.	Uranium nitrate				22	22	0						
17.	Magnesium chloride				23	23	0						
18.	Uranium nitrate	24	24	0									
18.	Magnesium chloride	24	24	0									
19.	Calcium chloride	25	25	0									

Judging from table 5(b), for natural pH, calcium orthophosphate, calcium citrate, calcium lactate and thorium nitrate are in the first class followed by calcium oxide, aluminum potassium sulfate and magnesium oxide in the second class, sulphur dioxide only, calcium chloride, uranium nitrate and magnesium chloride in the fourth class. Third class is missing when L.S.D. at the 5% level of 5.47 is taken into consideration. They are rated in the descending order as above for brine-cracking of cherries.

In case of the controlled pH of 3.0, the arrangement is different. Calcium orthophosphate, magnesium chloride, sulphur dioxide only, calcium chloride, calcium citrate, aluminum potassium sulfate, magnesium oxide, calcium lactate, and calcium oxide fall in one and the same class statistically, followed by thorium nitrate in the second and uranium nitrate in the third class. They are rated in the declining order as above for brine cracking of cherries.

The above orders of ratings give a fair picture of the cations and also the anions under the variables of pH.

Correlation of Firmness to the Cracking of Brined Cherries:

Both the firmness and freedom from brine-cracks are important industrially; the latter being a little more important than the former. Less firm or soft cherries can be processed into Maraschino cherries, and still bring some

money, though not at premium rates, whereas cracked

cherries are unfit for this purpose.

With the above in view, a correlation between these

two was calculated. It was found that the regression of

cracked cherries on the firmness as measured by Penetro-

meter pressure readings was 0.17 cracks per increase of

one unit in pressure-test readings. A correlation (r^2)

of 0.476 was found between the number of cracked cherries

and the pressure readings. The "N" in this case was 44.

It means that for every 100 penetrometer pressure units,

there were 17 cracked cherries per 25. This is an over-

all picture for all the treatments under the variables

of pH and storage temperatures and does not apply to

individual treatments as such.

It is difficult to evaluate all these treatments

under the aforementioned variables in regard to firmness

and brine-cracking together. It is, however, clear from

table 3 that calcium orthophosphate under these variables

(over-all effect) gave the best results followed by cal-

cium citrate, next in order are calcium lactate, calcium

oxide, and aluminum potassium sulfate. The other treat-

ments are not important. It is emphasized, however, that

for each set of conditions, the order of rating in regard

to firmness and brine-cracking would be different. There-

fore, no general conclusions can be drawn except as pre-

sented in table 3.

In spite of the regression and the correlation of firmness and brine-cracking, there seems to be much variation between the individual treatments. Some of the treatments which give firm cherries allowed an appreciable number of cracked cherries and similarly some of the treatments which gave very soft cherries were either completely devoid of or had some cracked cherries. This is clearly seen from tables 7 and 8 (appendix).

These factors affecting brine-cracking are in agreement with those of Cruess (26, p.280).

Role of Individual Factors in Affecting the Firmness and the Brine-Cracking of Cherries:

The purpose of other analytical data, besides the major factors like chemical treatments, pH and temperature, was to determine if they had any effect on the firmness and brine-cracking of cherries. These factors are discussed below:

a) Total Sulphur Dioxide After Storage: As shown in table 10 (appendix), with a few exceptions, in which total sulphur dioxide was low after storage, the total SO_2 was practically the same in most of the treatments. Since the fruit jars used were tightly sealed, there was no loss of SO_2 by volatalization. The reduction in most cases was due to the bleaching and complex reactions of cherries,

SO_2 and the chemicals used. In the few exceptions, particularly in case of thorium nitrate, (at natural pH and at room temperature), the loss may have been due to undetected leaks, where the loss was due to volatalization. This was the only case in which the spoilage due to decomposition as a result of lack of SO_2 or due to microbes, was noticed. As a general rule, there was less loss of total SO_2 in the cold storage than at room temperature storage. The final total SO_2 does not seem to have a direct effect on the firming or brine-cracking of cherries. This, along with free SO_2 treatments, initial pH and storage temperatures may be responsible for the differences between the bleaching actions as noticed from table 9 (appendix). Similar observations were also made by Atkinson and Strachan (6, p.142). Its main effect seems to be on that of bleaching of cherries and the resultant pH.

b) Free Sulphur Dioxide After Storage: Free SO_2, while less than total SO_2 closely paralleled it. This is more responsible than total SO_2 for the preservation of the fruit, although mainly dependent upon the latter. As for the rest of the reactions, exceptions are the same as those given for total SO_2.

c) Final pH: Judging from table 10 (appendix), there seems to be a trend for the final pH to be slightly higher in room temperature storage than in cold storage, with a

few exceptions. This seems to be a function of total and free SO_2 concentrations, the initial pH, the kind of treatments and storage temperature. No single resultant pH can be stated to be the best. It depends on the chemicals used. This is shown by the significant interactions in both tables 4 and 5. It, however, seems that brine-cracking of cherries is affected more than the firmness by the resultant pH. There seems to be a wide range of the resultant pH, where cherries of good quality in regard to firmness and brine-cracking are obtained and yet within this range, there are a few exceptions which have given very soft and also cracked cherries. On the other hand, others have given very soft but fewer or no cracked cherries, as would be clear from table 10 (appendix).

It seems that cherries below the resultant pH of 2.68, more specifically between 1.69 to 2.25 or even up to 2.40, were very soft and badly cracked and the damage ranged from 60 to 100 %. For mild to fair cracking, pH was over 2.60 and up to 3.0. Most of good results were obtained in the pH range of 3.1 to 4.1. On fresh solution basis, the critical initial pH was below 2.40. It therefore, is evident that each chemical as used in these experiments has a different optimum pH or the range of pH. The initial control of pH is much more important as it controls the resultant pH and other factors mentioned before. These findings

are in fair agreement with those of Cruess (26, p.280) but
are in contrast to those of Wiegant et. al. (88, pp.93-
100), Woodroof and Cecil (91, pp.10-11), Atkinson and
Strachan (6, p.142).

Evidently this variability in the optimum pH or range
of pH as given by different investigators is due to the
different chemicals and different concentrations used in
conjunction with different concentrations of SO_2 solutions,
initial pH or the amounts of acids present in the cherries,
the latter varies depending upon climatic, soil, cultural
practices and stage of maturity. Although pH is not the
linear function of the quantity of acids or bases, it is
definitely affected by their concentration and the ratios
in which they are mixed.

d) <u>Temperature</u>: Temperature of storage by itself has no
direct effect on the firming or brine-cracking of cherries.
It affects firming only through its interactions with
treatment and pH, but for brine-cracking, it has no affect
even through its interactions with the above variables.
This is shown in tables 4 and 5. These observations are
in contrast to those of Ross (70, pp.40-42), but are in
agreement with those of Bullis and Wiegand (17, p.8) and
Atkinson and Strachan (6, p.142).

e) <u>Chemical Treatments</u>: No single explanation is appar-
ent for the permeability and ion exchange, the brine-

cracking or softening of the cherries. The fact that the permeability is affected by different treatments is shown by the differences, even though slight, in the intake of different elements by the cherries treated with their respective salts, and in the loss of total and soluble solids. These findings substantiate the theory of permeability as affected by different elements, cations and anions.

Raber (69, pp.298-308) explains these differences on the basis of electrical condition of the membrane which in turn is affected by cations, anions and certain specific ions like chlorides, OH^- or H^+. This is also affected by other variables like pH and temperature. The theory of valence, as given by several authors, also holds good to quite an extent. Taking specific cases of calcium orthophosphate and calcium citrate, which are the first two best treatments, Raber states that these ions with the largest charges have the most influence, which explains why citrates have a greater "salting out" effect than monovalent anions like chlorides and nitrates. He also states that sulphate, tartarate, citrate and acetate cause a shrinking, while chloride, bromide and nitrate cause a swelling. This is very clear in these experimental trials, when calcium and magnesium chlorides, thorium and uranium nitrates caused swelling and rupture of the skins, whereas,

aluminum potassium sulphate, calcium citrate, calcium orthophosphate did not to the same extent. Atkinson and Strachan (6, pp.141-144) are also of the same opinion as Raber in connection with OH⁻ and chlorine ions and their role in firming and cracking of brined cherries.

Another good explanation for brine-cracking of cherries is given by Bullock (18, pp.243-253) who states that cracking is the result of permeability, osmotic concentrations and pressures due to sugars and pectic substances and the swelling of other colloidal substances. Elasticity and plasticity of cells as suggested by some of these authors are naturally affected by these treatments, which in turn affect the firmness and cracking of cherries. The explanation of the valence difference, as suggested by some authors, did not hold good in these series of trials for thorium and uranium salts due to the fact that their concentration was too high. According to Bullock (18) and others, the effect of valence is noticeable only when the salts are in dilute solutions.

The results do not agree with the statement of Atkinson and Strachan (4, pp.72-74), which is, "The resulting hardening or firming of the tissue is accomplished to the same extent with different calcium compounds if the content of the elemental calcium in the formula is the same regardless of the compound used." All the calcium salts

and other mineral elements were used in these trials on same calcium levels with that in calcium oxide, but firming, and brine-cracking as judged by the pressure test readings and number of cracks were not the same. The electrical charges carried both by cationic and anionic part of the chemical would explain this difference. The anions may act directly as such, but the general conception is that they give some kind of buffering action for the cationic part of the salt for reaction with other materials and this seems to be justified by these trials. (18) This also includes the dissociation of different salts.

f) Total Solids: Table 11 shows the data for total solids. Fresh cherries initially had 19.024% total solids. As a result of brining operations with different chemicals, there was a reduction of total solids to about 9 to 14% in the various treatments. The loss of total solids does not affect either the firming or the brine-cracking materially as an over-all picture. There seems to be a general trend toward less loss of total solids in the treatments controlled at pH 3.0 than at their natural pH. There are a few exceptions as are shown in table 11. This leaching effect is mostly dependent upon the number of cracks in the cherries, which in turn are the function of pH and the interaction of treatment x pH. Since the pH of 3.0 made a significant difference as is shown in table

5(a), the less loss of total solids in this case seems justified. The cherries, which were externally cracked, lost more total solids as compared to internally cracked cherries, which are called brine-checks by some.

g) Soluble Solids: Fresh cherries had 17.5% of soluble solids initially. There was a reduction of soluble solids to about 9 to 13% due to different treatment. Losses of soluble solids with a few exceptions as are given in table 11 closely paralleled losses of total solids. Other observations, exceptions, and theories explaining the losses are just the same as those for total solids. Comparing the soluble solids in the brined cherries with those in their respective brines, they are either practically the same or very close to each other, showing that the cherries and brine had come to an equilibrium.

Loss of total and soluble solids explains the phenomenon of permeability as affected by cations and anions, pH, etc., and has been discussed before.

h) Mineral Elements: Besides the losses in total and soluble solids, the increase in mineral elements in differently treated brined cherries support the phenomenon of permeability and ion exchange.

Calcium: Calcium was determined in fresh cherries and in those treatments in which calcium salts were used as hardening agents. Judging from table 15 (appendix), it appears

that there was some gain in the total calcium in all the treatments over that of fresh cherries, which had 0.134% on fresh weight basis and 0.743% on dry weight basis. There is no important difference between the treatments which gave firm and in most cases less cracked cherries and the ones which gave soft and more cracked cherries in regard to total calcium gain. It only shows that cherries have picked up some calcium in these treatments irrespective of its any apparent effect in the firming or cracking of cherries. The difference, though insignificant in the ordinary sense, may in terms of molecules be significant. Magnesium: Magnesium, like calcium, was determined only in fresh cherries and those treated with magnesium salts. The results are expressed on milligram per cent basis (i.e. mgm per 100 grms. of cherries) in table 15 (appendix).

The results are self explanatory. Cherries have picked up some magnesium in the treated brines. There was more gain by the cherries treated with magnesium chloride than those treated with magnesium oxide; though the latter gave better results as regard firming and less brine-cracking. This clearly shows the action of chloride ion and also OH⁻ ion, and the effect of concentration of the two salts on weight basis, on firming and brine-cracking of cherries.

Aluminum: Aluminum was determined in fresh cherries and

the cherries treated with aluminum potassium sulphate. The results are expressed like magnesium in milligrams per cent and are given in table 15.

There was a considerable gain of aluminum in cherries treated with this salt brine in both levels of pH, but it was greater at the controlled pH of 3.0. The latter treatment produced firmest cherries, although it gave 25% internally cracked cherries. At the natural pH of 1.68, cherries were soft with 48% of them cracked and the rest of them were shrivelled and wrinkled.

Although the cherries gained more calcium on the weight basis, on the number of times basis, they gained several fold in other elements of higher valence like aluminum. This may explain the effect of valence on permeability as postulated by several authors and cited before. As Bullock (18, pp. 243-253) states these different cations reduce the permeability of the cell membrane by combining with the exposed carboxyl groups of the pectinicous substances; divalent and trivalent ions by tieing two or three molecules and replacing hydrogen as compared to a univalent ion. This holds good in the majority of these trials, as other factors like concentration, pH etc., override it.

i) Pectic Substances:

Alcohol insoluble solids (A.I.S.): The results are

given in tables 12 and 13 (appendix). On the dry weight
basis, for fresh cherries, A.I.S. was calculated on the
basis of of 19.024% total solids, whereas for brined
cherries from their respective total solids, which were
much lower by about 6 to 10 % than the fresh cherries due
to the leaching effect. There is a wide range of A.I.S.
in different treatments. In some cases, A.I.S. on fresh
as well as on dry weight basis is more than the fresh
cherries. The A.I.S. in cherries treated with SO_2 only
is less than in fresh cherries. This shows that some of
the A.I.S. in the fresh cherries have been rendered sol-
uble by the action of sulphur dioxide solution. Since
the action of sulphurous acid with respect to its concentra-
tion is common in all the treatments, the other variabil-
ity of higher A.I.S. in certain treatments than in fresh
cherries is primarily due to the chemicals used or their
complex interaction with sulphurous acid and cherries.
There seems to be a trend for A.I.S. to be higher than
2.30% (on fresh weight basis) to as much as or even high-
er than A.I.S. in the fresh cherries, in those treatments
which gave firmer cherries and in most cases also fewer
cracked cherries. The only exception to this is magnesium
oxide (natural pH at room temperature). Those treatments,
which gave soft and also more cracked cherries had A.I.S.
around 2.0% and in most cases, less than 2.0% on the fresh

weight basis. On dry weight basis, all the treatments
had higher A.I.S. than the fresh cherries (13.204%).
Those treatments, which gave soft and also, in most cases,
more number of cracked cherries, had about 18.0% A.I.S.
with the exception of magnesium oxide (natural pH at room
temperature) which gave abnormally high A.I.S. of 27.899%.
In case of the treatments giving firm cherries and in
most cases fewer number of cracked cherries, A.I.S. was
over 21%; most of them had between 22 to 24.5 %, with
the only exception of calcium lactate (controlled pH of
3.0 at room temperature), which had 16.9% A.I.S. This
exception of calcium lactate treatment is due to the fact
that there was the least loss of total as well as soluble
solids as compared to any other treatment.

These trends are applicable more to the firmness or
the softness of the cherries than to the brine-cracking,
though in majority of the cases, they hold good for brine-
cracking as well.

Protopectin: Judging from tables 12 and 13 (appendix),
there seems to be a sort of general tendency for proto-
pectin to be less in those treatments which give firm and
in most cases, also fewer cracked cherries as compared to
the other opposite case, with the exceptions of calcium
lactate (controlled pH of 3.0) and aluminum potassium
sulphate. This is on fresh weight basis. Very similar

results were obtained, when protopectin was calculated as % of A.I.S. On dry weight basis, these trends are more explicit and very similar to the above.

The above is indicative of the fact that there is something else besides protopectin or total pectin in A.I.S. which is taking a vital part in the phenomenon of firming and brine-cracking of cherries.

Soluble Pectin: Though soluble pectin is found in very small amounts, it shows, however, a trend for being more in those treatments, which gave firmer and in most cases fewer cracked cherries than the other case. The exceptions to this are clearly seen in the tables 12 and 13 (appendix). Some of them are borderline cases. The same holds good when soluble pectin was calculated as per cent of A.I.S. and likewise when it was calculated on dry weight basis as such or as per cent of A.I.S.

It was also observed while comparing the same treatment, under its natural pH and controlled pH of 3.0, that the latter had more soluble pectin than the former in all the treatments, both on fresh and dry weight basis. The same holds good, when it was calculated as per cent of A.I.S. This was not found in case of protopectin.

Total Pectin: Total pectin, which is the arithmetic total of protopectin and soluble pectin, does not show any

conspicuous difference between the treatments, when calcu-
lated either on the fresh or dry weight basis. However,
when it is calculated as per cent of A.I.S. on dry weight
basis, there is a tendency toward higher values in those
treatments which give soft, and in most cases, more crack-
ed cherries and lower values in the other cases. There was
a loss in total pectin in all the treatments.

These are just the trends and may not be statistically
significant.

Interrelationships of Pectic Substances: These are given
in table 14 (appendix). The ratio of total pectin to pro-
topectin was found to be higher in those treatments which
gave firm and, in most cases fewer cracked cherries. For
other treatments this ratio was lower than for fresh cher-
ries. There were a few exceptions to this effect when the
conditions in regard to treatment, pH and temperature did
not favor the hydrolysis of protopectin to soluble pectin.
For the former case, excluding the exceptions, the ratio
varied from 1.23 to 1.87; for the latter case, it varied
from 1.00 to 1.22.

The ratio of total pectin to soluble pectin gives
rather a clearer picture and the results seem to be more
significant than the ratio of total pectin to protopectin.
With a few exceptions, as are clear from the table, this
ratio in the treatments giving soft and, in most cases,

more cracked cherries was very high, varying from 11.00 to 26.96.

The last ratio is for magnesium chloride at natural pH of 1.30, which gave the softest and 96% cracked cherries. This range of ratios is much higher than the 6.74 found for fresh cherries. In the case of treatments giving firm and in most cases fewer cracked cherries, the ratio was from 2.15 to 5.38 with the exception of a border line case.

Since total pectin is the arithmetic total of protopectin and soluble pectin, the ratio of protopectin to soluble pectin is less by 1.00 than the ratio of total pectin to soluble pectin in all cases.

It appears that the interrelationships of the pectic substances are upset by the different treatments. These interrelationships of pectic substances give a better picture of the effects of treatments than the total amounts of the pectic substances.

Role of Pectic Substances in Firming and Cracking of Cherries:

As regards the role of pectic substances in the firming of and preventing of cherries from brine-cracking, it is more a matter of speculation than on experimental proof. This is evident from the diversity of opinions cited in the literature review. Different methods were

employed by several investigators for determination of
pectic substances. They assumed these to be identical,
but others (61, 60) proved it to be seperate entities.
Even the existence of parent substance, protopectin, is
doubted (47, p.213). Furthermore, there are no definite
boundary lines between pectic substances themselves and
hemicellulose and celluloses. The pectic substances,
however, are held responsible for firming and cracking of
fruits. There are still other little understood reactions,
also important in this connection, as was found in case of
alcohol-insoluble solids in these trials (47, pp.544-545).
Some investigators believe that the firmness of the fruits
is due to protopectin and calcium pectate, whereas other
investigators attribute the firmness of the fruit to cal-
cium pectate only (41, pp.41-42; 52, pp.499-508). There
are still other cases like pears and sweet potatoes, in
which there is a gain of protopectin instead of a loss by
its hydrolysis (27, pp.29,69,70; 41, p.42). Lack of de-
pendable means, other than quantitative, of evaluating
these pectic changes, and the lack of knowledge of comp-
osition or structure of pectic substances adds to the
difficulties. The quantities of calcium pectate may be
the same in two samples and yet they may show a wide
range of colloidal properties (47, p.547). This was very
clearly seen in these experimental trials.

It is possible in case of aluminum potassium sulfate treatment, when more total pectin was found than in fresh cherries on dry weight basis, that soluble pectin was received from another source besides from the hydrolysis of protopectin. During the process of solubilization of protopectin, fissure of some of the linkages involving carboxyl groups occurred, and the existence of this trivalent ion Al^{+++} in bonding pectic or pectinic acids into protopectin is another possibility. (47, p.55). If the amounts of cellulose, hemicellulose and proteins, which form complexes with pectic substances had been determined, a clearer picture of these changes probably would have been obtained (41, pp.40-41). This trend was shown by the A.I.S. in the treatments giving firmer and fewer cracked cherries. The possibility of incorporation of the above constituents and other carbohydrates like arabans and galactans ("ballast") in A.I.S and their effect on firming and cracking of cherries cannot be ruled out (47, 61).

Cherries, which are likely to crack, have a higher proportion of pectic substances than those which do not crack (43, pp.769-771). Partial hydrolysis of protopectin, and that part of it which is combined with cellulose, and cellulose by itself increase the degree of hydration and swell till a maximum capacity is exceeded, causing the skin of the fruit to burst (47,p.184). This

was the only thing found quantitatively in these trials.
The explanation for this is that the conditions of pH,
concentration and kind of chemicals and SO_2 solution were
such that they did not hydrolyze pectic substances to the
degradation products, which would give soft and more crack-
ed cherries. As a result of this swelling and osmotic
pressure, skins of cherries burst or cracked.

The data of pectic substances are in fair agreement
with some authors (51, pp.32-34; 47, p.299; 53, pp.8-12)
but not with Conrad and Bertsch (25, p.2672), whose fig-
ures are very high. It is true that cherries are low in
useful pectin (47, p.528) as other fruits give a better
and quicker response to calcium treatments.

Further discussion is made on the following popular
hypothesis given by Baier[1]. The opinions of different
investigators in favor of or against it are given.

> When cherries are in different brines for some time
> with SO_2 solution, it is assumed that enzymatic
> changes (protopectinase, pectin esterase, poly-
> galacturonase) as affected by the treatments and
> the conditions of pH, temperature, etc., will have
> taken place, some of which would go in the direc-
> tion of demethylation and the resulting degrada-
> tion products would be less soluble in the pre-
> sence of say calcium or other cations, than at an
> earlier stage. Still earlier in the history of
> cherries, the pectin would be in the form of so
> called protopectin. Considering the progression
> in the forward direction, first the pectin which
> is mostly in the form of protopectin tends to
> split theoretically into cellulose and soluble
> pectin, but the soluble pectin tends to become

[1]Baier, W. E. Personal letter to the author. 1950.

demethylated and depolymerized. The demethylated
part becomes less soluble in the presence of cal-
cium or other cations depending upon the treat-
ments, while the depolymerized part becomes more
soluble.

Calcium and magnesium are absorbed by protopectin
rather than combined in stoichiometrical formation of
salts with free carboxyl groups (47,p.74). The possibil-
ity exists of ions like aluminum linking polygalacturonic
acid units into higher structures and resembling protopec-
tin and giving similar characteristics (47, pp.75-76; 57,
pp.34-38; 14, p.418). Insolubility of protopectin, due to
its association with cellulose or the presence of poly-
valent ions, its large molecular size and combination of
these factors, is affected differently by these treatments
which may be the cause of firming or softening. The degree
of demethylation (31, p.20), the pH range of the medium
affecting the rate of hydrolysis of protopectin to soluble
pectin and degradation products (58, pp.42-44) along with
the effect of temperature and non-uronide material are
likely to affect firming and cracking of cherries.

Degree of demethylation and deesterification is
affected by these treatments, which in turn affect the
jellying power (61). Several authors (79; 40; 89; 31)
favor the view that the jellying power of pectinic acids
decreases with decreasing methoxyl value, whereas, others
(58; 59; 57; 55; 56) believe that it is not affected by

methoxyl value or degree of esterification, but is depend-
ent upon degree of depolymerization (molecular weight).
Others (61, p.32) believe that methoxyl value parallels
the chain length and consequently affects the gel forming
characteristics. These unfortunately were not determined.
Demethylation, deesterification, decarboxylation and de-
polymerization and the variation in these due to the treat-
ments, will give a better picture than the quantities of
pectic substances.

The effect of pH and the range of pH , where good
results are obtained, are in agreement with those of
Kertesz (47, p.197).

The loss of total pectic substances in SO_2 solution
confirms the results of some authors (24; 22; 23, pp.119-
121).

The gel characteristics as affected by the concentra-
tion of pectic substances and other factors, reviewed at
length in literature review, partly explains these differ-
ences in firmness of cherries (47, p.164; 12, pp.12,36,37).

Various pectinic acid preparations have different pH
maxima. They are affected by the kind of treatments, temp-
erature, concentration, degree of demethylation, depoly-
merization, deesterification, etc.

Temperature by itself did not have any effect on the
firming or cracking of cherries. This is justified by

Kertesz's statement (47, p.147) that the pectinic acids of low viscosity or those artificially degraded show the lack of temperature sensitivity even at higher concentrations. The effect of temperature is indirect through other factors as mentioned before. Low temperature storage aids in methylester retention (14, p.420; 62, pp.16,147-149; 59, p.36; 14, p.420).

Several investigators have given other explanations in favor of or against this hypothesis. Some of these have been cited before in the section of "Review of Literature".

Up-setting the interrelationships of pectic substances due to different treatments, which would involve the phenomenon of the change of permeability and osmotic pressure, is a very likely cause of these changes in the tissue characteristics of cherries.

Similar observations were made by the author in grapes while working at F. M. Ball and Company, Oakland, California in 1949. Grapes in the early season, when they have more of protopectin, split badly (about 90%) when canned as a part of fruit cocktail or as such in a syrup of 45 to 55%. Dipping treatments in the dilute solutions of calcium oxide, calcium chloride and calcium citrate with and without thorough rinsing with water resulted in giving from 0 to 15 % of splitting. On analysis by the National

Canners Association Research Laboratories, San Francisco, it was found that there was either no increase or 1 or 2 p.p.m. increase of calcium over the control, which originally had 28 p.p.m. This may support the theory of absorption of calcium or in some way combining with the protopectin to give this protective action against splitting.

Different treatments result in varying degrees of demethylation of protopectin. Demethylated part of protopectin combines with the cationic part of the salts and gives the corresponding pectates and pectinates. This is another possible explanation for firmness or softness of cherries.

The above process may be simultaneous. There is practically no difference in protopectin, calcium pectate and calcium pectinate as regards their solubility behavior and reaction with acid and base under these experimental conditions (45, p.12; 46, p.26; 52, pp.499-508; 47, pp.555-556). The results are in harmony with those of Esslen, Hart and Fellers (29, pp.12-13) for the range of pH for good firm cherries; with Kertesz (47, pp.37-38, 42) for superiority of calcium lactate salt in firming of fruits and inferiority of calcium and magnesium chlorides with others (35, pp.42-43; 28, pp.11-12).

Baker (13, pp.197-198) has given an excellent explanation of the role of calcium salts in firming of apple

slices (given in literature review) which holds good in
the brined cherries to quite an extent.

Obviously the effects of different treatments on the
firmness and brine-cracking of cherries is more of qualita-
tive than of quantitative nature. (pertaining only to
those items which were determined)

Better results are obtained if the fresh cherries are
exposed to a very dilute solution of alkali or acid for
some time and then further exposed to dilute solutions of
the firming agent itself. The mere exposing of fresh
cherries to the latter treatment (calcium salts of the
fruit acids, like citrate, malate, or even lactate, are
suggested) for some time, and then barreling with the
brine of sulphur dioxide solution with lesser concentra-
tion of the firming agent, will give a more uniform and
better product.

A patent to this effect is being sought by the author
and his associate, Allen Phillips, manager, The Dalles
Cooperative Growers, The Dalles, Oregon. The last men-
tioned experiments were conducted at The Dalles during the
summer of 1953.

The plausible theory behind the above work is that
exposure of fruit to a very dilute solution of alkali or
acid for some time results in deesterification and de-
methylation of the pectin in the fruit. This affords

better chances for such pectin to react with the cationic part of the firming agent. Further exposure to brine solution (with the firming agent present) will eliminate the chances of the soluble pectin or even protopectin being hydrolyzed to degradation products at a faster rate than the firming agent can combine with them to form corresponding pectates or pectinates.

In the above experiments, the rate of deesterification, demethylation and hydrolysis in general are controlled. This is substantiated by Kertesz's work (47) which shows that more useful pectin is obtained for jellification by hydrolyzing the protopectin with alkali or acid than by enzyme. The former are random in nature and the latter regular.

CHAPTER V

SUMMARY

1. A study has been made of the effect of cations and
    anions, using some of the groups of the Hofmeister
    series in the form of salts at two different acidities
    for each salt (one at the pH resulting from the addi-
    tion of the salt and the other at an adjusted pH of
    3.0) and two different storage temperatures (room tem-
    perature of about 70°F., and 40°F.). The salts used
    in these trials were: calcium oxide, calcium lactate,
    calcium chloride, calcium orthophosphate, magnesium
    oxide, magnesium chloride, aluminum potassium sul-
    phate, thorium nitrate and uranyl nitrate.

2. The following tests were made after one year's storage
    to study the effect on the firmness and cracking of
    brined cherries: firmness test, number of brine-
    cracks, color, free and total sulphur dioxide, pH, sol-
    uble and total solids, pectic substances and certain
    mineral elements. Statistical analysis was also made
    to measure the effect of treatments, pH and temperature
    of storage on the firming and cracking of brined
    cherries.

3. Some suggestions are made for further studies. For
    instance, it is suggested that the degree of demethy-
    lation, deesterification, and depolymerisation probably

would give a better picture for the phenomenon of firming and cracking of brined cherries than the trends shown by the pectic substances in these trials.

CHAPTER VI

CONCLUSIONS

Under the conditions of the experiments reported herein, the following conclusions may be made regarding the firmness and cracking of brined Royal Ann cherries.

1. Factors which affect the firmness of brined cherries significantly (statistically) are treatments with specific salts, pH, the interactions of treatment x pH, treatment x temperature, and treatment x temperature x pH. The two temperatures of storage as used in these studies, by themselves or their interaction with pH, do not affect the firmness of brined cherries.

2. Factors which affect the cracking of brined cherries significantly (statistically) are pH and its interaction with treatments. The two temperatures of storage and the specific treatments used in these trials by themselves and other interactions do not have any significant effect on the cracking of brined cherries.

3. A correlation $(r)^2$ of 0.476 was found between the number of cracked cherries and the pressure readings. High pressure readings signify more softness and, in most cases, more cracking.

4. The following salts are arranged in the descending order of their beneficial effect on firming and less brine-cracking of cherries: calcium orthophosphate, calcium citrate, calcium lactate, calcium oxide and aluminum potassium sulphate. Other salts were not so beneficial as the above salts.

5. As an over-all effect for all treatments, solutions initially controlled at pH 3.0 gave better results than the pH resulting naturally from the addition of the salts in regard to firmness and cracking of brined cherries.

6. The resultant pH in most cases was higher after storage than when the cherries were brined in the beginning, due to reaction with cherries. There was a tendency for the resultant pH to be slightly higher when the cherries were held at room temperature than in cold storage. It seems to be the function of total and free SO_2. The effect of pH seems to be more pronounced on brine-cracking than on the firmness of cherries. The ranges of pH found for good, fair and poor cherries are 3.1 to 4.1; 2.68 to 3.0 and less than 2.60 respectively.

7. Total and free SO_2 do not affect firming or brine-cracking of cherries directly, although they may indirectly, through their role in regulating pH and

other complex reactions. As a trend, there was less
loss of total as well as free SO_2, in the cold storage
than in room temperature storage.

8. Depending upon the treatments, there was a reduction
of total solids to about 9 to 14 per cent from 19.024
per cent, which was originally present in fresh
cherries. This loss was less in the treatments
initially controlled at pH 3.0 than at natural pH
(over-all effect). In externally cracked cherries,
there was a greater loss of total solids than in
internally cracked cherries.

9. The reduction of soluble solids from 17.05 per cent
in fresh cherries to 8.7 to 13.4 per cent due to
treatments, closely parallels the reduction in total
solids.

10. The loss in total as well as in soluble solids coupled
with the gain of elements by the cherries substanti-
ates the theory of permeability and the factors
affecting it.

11. The alcohol-insoluble solids in firm brined cherries
tended to be higher than 2.3 per cent. In some cases
it was even higher than in fresh cherries. Soft and
cracked cherries had less than two per cent of
alcohol-insoluble solids on fresh weight basis. On
dry weight basis, the former had over 21 per cent and

the latter had less than 18 per cent.

12. The protopectin content tended to be less in cherries which were given treatments resulting in more firm and fewer cracked cherries than in soft and cracked cherries, both on the fresh and dry weight bases. This also held true when it was calculated as per cent of alcohol-insoluble solids. Soluble pectin, however, tended to be greater in the cherries which were more firm and had fewer cracks. It was also found to be greater when the brine was originally adjusted to pH 3.0 than when the natural pH of the salt solution prevailed. Total pectin or its loss due to treatments did not affect the firmness or brine-cracking of cherries. The ratio of total pectin to protopectin was higher in firm and fewer cracked cherries than in soft cherries. The range was from 1.23 to 1.87 in the firm cherries and 1.00 to 1.22 in soft and cracked cherries. In the former case, the ratio of total pectin to soluble pectin varied from 2.15 to 5.38 and in the latter case, it was very high and varied from 11.00 to 26.96.

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APPENDIX

Table 7.

The effects of different salts in the brine at natural and controlled pH of 3.0 after storage for about one year at room temperature (70° F.) on the firming and brine-cracking of cherries.

Serial No. of treatments	Treatments	Initial pH of brines	Penetrometer pressure readings with range (average of 25 cherries)		No. of brine cracks out of 25 cherries with range	
			Pressure test readings	Range	No. of cracked cherries	Range (length in inches)
1.	Fresh cherries	3.88	7.66	0-15.5	-	-
2.	Sulphur dioxide only (natural pH)	1.62	26.48	13-38	20 ext.	1/4" - all over
3.	Sulphur dioxide (controlled pH)	3.00	23.44	10-40	-	-
4.	Calcium oxide (natural pH)	2.40	11.96	4-21	8 int.	1/4" - 1"
5.	Calcium oxide (controlled pH)	3.00	11.44	8-21	1 int.	1/4"
6.	Calcium lactate (natural pH)	2.80	11.48	7-16	2 ext.	1/4" - 3/4"
7.	Calcium lactate (controlled pH)	3.00	10.24	5-14	2 int.	1/4" - 1"
8.	Calcium chloride (natural pH)	1.34	29.16	14-45	25 ext.	1/4" - all over
9.	Calcium chloride (controlled pH)	3.00	13.28	5-31	-	-
10.	Calcium citrate (natural pH)	2.68	11.00	6-18	1 ext., 2 int.	1/4" - 1/2"
11.	Calcium citrate (controlled pH)	3.00	9.32	3-19	3 int.	1/4"

Table 7. (Continued)

The effects of different salts in the brine at natural and controlled pH of 3.0 after storage for about one year at room temperature (70° F.) on the firming and brine-cracking of cherries.

Serial No. of treatments	Treatments	Initial pH of brines	Penetrometer pressure readings with range (average of 25 cherries)		No. of brine cracks out of 25 cherries with range	
			Pressure test readings	Range	No. of cracked cherries	Range (length in inches)
12.	Calcium orthophosphate (natural pH)	2.52	11.52	4-19	-	-
13.	Calcium orthophosphate (controlled pH)	3.00	9.48	6-19	-	-
14.	Magnesium oxide (natural pH)	6.34	13.32	5-19	4 ext., 5 int.	1/4" - 1/2"
15.	Magnesium oxide (controlled pH)	3.00	16.24	9-31	2 int.	1/4" - 1/2"
16.	Magnesium chloride (natural pH)	1.30	30.32	19-41	24 ext.	1/4" - all over
17.	Magnesium chloride (controlled pH)	3.00	20.04	8-34	4 int.	1/4" - 1/2"
18.	Aluminum-potassium sulphate (natural pH)	1.68	15.68	9-27	12 ext.	1/4" - 1/2"
19.	Aluminum-potassium sulphate (controlled pH)	3.00	8.08	4-11	5 int.	1/4" - 1/2"
20.	Thorium nitrate (natural pH)	1.36	20.76	14-31	7 ext.	1/4" - 1"
21.	Thorium nitrate (controlled pH)	3.00	20.56	11-45	6 ext., 6 int.	1/4" - 1"
22.	Uranium nitrate (natural pH)	1.48	22.96	10-53	24 ext.	1/2" - all over
23.	Uranium nitrate (controlled pH)	3.00	19.84	9-35	7 int.	1/4" - 1 1/4"

Table 8.

The effects of different salts in the brine at natural and controlled pH of 3.0 after storage for about one year at cold storage temperature (40° F.) on the firming and brine-cracking of cherries.

Serial No. of treatments	Treatments	Initial pH of brines	Penetrometer pressure readings with range (average of 25 cherries)		No. of brine cracks out of 25 cherries with range	
			Pressure test readings	Range	No. of cracked cherries	Range (length in inches)
1.	Fresh cherries	3.88	.7.66	0-15.5	-	-
2.	Sulphur dioxide only (natural pH)	1.62	21.56	13-33	17 ext.	1/4" - 1/2"
3.	Sulphur dioxide (controlled pH)	3.00	25.72	8-45	4 ext., 1 int.	1/4" - 1/2"
4.	Calcium oxide (natural pH)	2.40	10.80	5-14	3 ext., 8 int.	1/4" - 3/4"
5.	Calcium oxide (controlled pH)	3.00	10.52	3-19	8 int.	1/4" - 1/2"
6.	Calcium lactate (natural pH)	2.80	13.60	7-20	5 int.	1/8" - 3/4"
7.	Calcium lactate (controlled pH)	3.00	13.04	6-21	6 int.	1/4" - 3/4"
8.	Calcium chloride (natural pH)	1.34	20.84	12-31	18 ext.	1/4" - all over
9.	Calcium chloride (controlled pH)	3.00	13.64	9-20	5 int.	1/8" - 1/4"
10.	Calcium citrate (natural pH)	2.68	14.36	8-19	3 int.	1/2" - 3/4"
11.	Calcium citrate (controlled pH)	3.00	12.92	7-20	1 ext., 1 int.	1/6" - 1/2"

Table 8. (Continued)

The effects of different salts in the brine at natural and controlled pH of 3.0 after storage for about one year at cold storage temperature (40° F.) on the firming and brine-cracking of cherries.

Serial No. of treatments	Treatments	Initial pH of brines	Penetrometer pressure readings with range (average of 25 cherries)		No. of brine cracks out of 25 cherries with range	
			Pressure test readings	Range	No. of cracked cherries	Range (length in inches)
12.	Calcium orthophosphate (natural pH)	2.52	11.20	7-16	2 int.	1/6" - 1/4"
13.	Calcium orthophosphate (controlled pH)	3.00	9.68	6-14	1 int.	1/2"
14.	Magnesium oxide (natural pH)	6.34	20.60	12-26	12 ext.	1/2" - all over
15.	Magnesium oxide (controlled pH)	3.00	20.60	12-39	1 ext., 3 int.	1/8" - 1/2"
16.	Magnesium chloride (natural pH)	1.30	32.04	16-48	23 ext.	1/4" - all over
17.	Magnesium chloride (controlled pH)	3.00	20.32	13-37	-	-
18.	Aluminum-potassium sulphate (natural pH)	1.68	19.36	14-28	8 ext.	1/4" - 3/4"
19.	Aluminum-potassium sulphate (controlled pH)	3.00	10.92	5-15	-	-
20.	Thorium nitrate (natural pH)	1.36	15.40	10-24	4 ext.	1/4" - 3/4"
21.	Thorium nitrate (controlled pH)	3.00	12.12	5-18	12 ext.	1/4" - 1"
22.	Uranium nitrate (natural pH)	1.48	18.76	13-30	22 ext.	1/4" - all over
23.	Uranium nitrate (controlled pH)	3.00	20.08	6-38	2 ext., 10 int.	1/4" - 3/4"

Table 9.

Notes on the effects of different salts
on the color of brines and cherries.

Treatments*	Color of brines and the cherries with remarks.
1.	Just of the right color for brining.
2.	Majority of cherries white, others yellowish white. Very good color in case of cold storage. Lot of material leached out in brine as sediment.
3.	Straw-yellow. Excellent color.
4.	Straw-yellow. Excellent color. Some slightly pink.
5.	Straw-yellow - a little brownish. Classed as excellent, but slightly inferior to 4.
6.	Straw-yellow. Very good color. In cold storage, color was excellent.
7.	A little on the brownish side, classed as very good. In cold storage, color excellent.
8.	Decolorized to almost white, but in cold storage, color excellent.
9.	Straw-yellow. Excellent color, similar to 4.
10.	Straw-yellow. Excellent color, similar to 4 and 9.
11.	Very good except a few cherries unbleached pink. In cold storage, color excellent.
12.	Very good color. Cold storage sample excellent.
13.	Very good except a few with unbleached pink spots, white precipitate at the bottom of the jar in cold storage sample.
14.	Dull yellow with dark gray patches - not appealing to the eye, lot of white sediment at the bottom of the jar.
15.	Excellent - bright yellow.

Table 9. (Continued)

Notes on the effects of different salts
on the color of brines and cherries.

Treat-ments[*]	Color of brines and the cherries with remarks.
16.	Good, but on the whitish side, showing excessive bleaching. Cold storage sample excellent, but lot of solids leached out at the bottom of the jar.
17.	Very good except a few with pink spots.
18.	Pink, not bleached properly. Cracks were more of ruptured wrinkles type than splits.
19.	Very good in general except a few with pink spots.
20.	Pinkish yellow. Not well bleached. A thick layer of salt at the bottom of jar and salt firmly adhered to cherries.
21.	Excellent color of brine. A thick layer of salt at the bottom of the jar. Salt firmly adhered to cherries.
22.	Pinkish blue. Very unappealing. Blue salt sticking to cracked cherries. Most of the solids leached out.
23.	Fair - greenish yellow. In cold storage, color was comparatively better. Rest like 22.

[*] Refers to treatments given in Tables 7 and 8. Compare it for firming and brine-cracking of cherries from these tables.

Table 10.

Resultant pH, total sulphur dioxide and free sulphur dioxide (%)
after storage in different treatments.

Treatments[*]	Initial pH	Resultant pH		Total SO_2 %		Free SO_2 %	
		Room temp. (70° F.)	Cold storage (40° F.)	Room temp. (70° F.)	Cold storage (40° F.)	Room temp. (70° F.)	Cold storage (40° F.)
1.	3.88	–	–	–	–	–	–
2.	1.62	2.12	2.03	0.49	0.55	0.44	0.52
3.	3.00	4.08	3.92	0.47	0.51	0.42	0.45
4.	2.40	3.42	3.38	0.51	0.54	0.41	0.43
5.	3.00	3.64	3.43	0.47	0.56	0.38	0.48
6.	2.80	3.25	3.25	0.48	0.50	0.37	0.41
7.	3.00	3.48	3.39	0.49	0.52	0.38	0.43
8.	1.34	2.22	2.12	0.44	0.41	0.35	0.38
9.	3.00	3.70	3.00	0.47	0.49	0.40	0.35
10.	2.68	3.20	3.14	0.45	0.52	0.40	0.43
11.	3.00	3.32	3.39	0.46	0.53	0.40	0.43
12.	2.52	3.12	3.21	0.21	0.45	0.18	0.40
13.	3.00	3.76	3.57	0.45	0.48	0.35	0.42
14.	6.34	4.79	4.72	0.42	0.41	0.35	0.38
15.	3.00	4.02	3.98	0.43	0.44	0.33	0.36
16.	1.30	2.17	2.05	0.37	0.40	0.32	0.37
17.	3.00	3.62	3.58	0.42	0.45	0.36	0.32
18.	1.68	2.22	2.20	0.38	0.45	0.33	0.39
19.	3.00	2.71	2.68	0.42	0.46	0.35	0.40
20.	1.36	1.69	1.95	0.05	0.33	0.100	0.32
21.	3.00	3.58	2.50	0.44	0.42	0.40	0.35
22.	1.48	1.86	1.87	0.23	0.48	0.19	0.41
23.	3.00	3.91	3.62	0.44	0.57	0.39	0.44

[*] Refers to treatments given in Tables 7 and 8. Compare it
for firming and brine-cracking of cherries.

Table 11.

Total solids and soluble solids in differently treated brined
cherries after about one year storage at room temperature
(70° F.) and their correlation to firmness and brine-cracking.

Treat-ments*	Total solids by weight (%)	Soluble solids by hand-refractometer	
		In cherries (%)	In brine (%)
1.	19.0	17.5	-
2.	10.7	10.5	10.3
3.	9.3	8.7	9.4
4.	11.6	10.8	10.6
5.	13.1	12.5	10.6
6.	11.5	12.0	11.8
7.	13.9	13.4	13.0
8.	11.0	11.0	10.7
9.	10.9	11.0	11.0
10.	11.9	11.5	12.0
11.	11.6	11.5	12.5
12.	Not determined	-	-
13.	Not determined	-	-
14.	11.0	10.5	10.0
15.	11.6	11.5	11.0
16.	11.5	11.5	11.0
17.	11.6	11.8	11.5
18.	13.3	13.2	13.2
19.	13.3	13.0	13.0

* Refers to treatments given in Table 7. Compare it for
firming and brine-cracking of cherries.

Table 12.

Changes in pectic substances in differently treated brined-cherries
after about one year storage at room temperature (70° F.).

(Fresh weight basis)

Treatments*	Alcohol-insoluble solids (A.I.S.) %	PECTIC SUBSTANCES					
		Protopectin		Soluble pectin		Total pectin	
		%	% of A.I.S.	%	% of A.I.S.	%	% of A.I.S.
1.	2.522	0.138	5.510	0.024	0.959	0.163	6.489
2.	1.904	0.078	4.091	0.005	0.278	0.083	4.370
3.	1.544	0.052	3.381	0.011	0.738	0.064	4.119
4.	2.488	0.046	1.829	0.021	0.860	0.067	2.689
5.	3.152	0.054	1.701	0.037	1.161	0.090	2.862
6.	2.816	0.015	0.529	0.003	0.121	0.018	6.498
7.	2.352	0.058	2.462	0.027	1.161	0.085	3.622
8.	1.844	0.070	3.802	0.006	0.298	0.076	4.100
9.	1.900	0.020	1.032	0.017	0.900	0.037	1.932
10.	2.644	0.020	0.749	None	None	0.020	0.749
11.	2.700	0.028	1.052	0.010	0.382	0.039	1.433
12.	-	-	-	-	-	-	-
13.	-	-	-	-	-	-	-
14.	3.076	0.067	2.181	None	None	0.067	2.181
15.	2.032	0.041	2.018	0.004	0.182	0.045	2.200
16.	1.916	0.070	3.659	0.003	0.141	0.073	3.800
17.	2.104	0.071	3.612	0.008	0.361	0.084	3.973
18.	3.212	0.074	2.310	0.065	2.011	0.139	4.321
19.	2.232	0.076	2.352	0.066	2.039	0.142	4.391

* Refers to treatments in Table 7. Compare it for firming and
brine-cracking of cherries.

Table 13.

Changes in pectic substances in differently treated brined-cherries
after about one year storage at room temperature (70° F.).

(Dry weight basis)

Treat-ments[*]	Alcohol-insoluble solids (A.I.S.) %	Protopectin		Soluble pectin		Total pectin	
		%	% of A.I.S.	%	% of A.I.S.	%	% of A.I.S.
1.	13,204	0,728	5,511	0.127	0,960	0,854	6,471
2.	17.754	0.726	4,090	0.050	0,280	0.776	4,370
3.	16.683	0.564	3.380	0,123	0.740	0,687	4,120
4.	21.463	0.393	1.830	0.185	0,860	0.577	2.690
5.	24.080	0.409	1.700	0.279	1.599	0,689	2.860
6.	24.388	0.129	0.530	0,029	0.120	0.159	0,650
7.	16.900	0.416	2,460	0.196	1.160	0,612	3.620
8.	16.717	0.635	3.800	0.050	0,300	0.685	4,100
9.	17.360	0.179	1.030	0,156	0.900	0.335	1.930
10.	22,180	0.166	0.750	None	None	0.166	0,750
11.	23.200	0.244	1.050	0.088	0,380	0.332	1,430
12.	–	–	–	–	–	–	–
13.	–	–	–	–	–	–	–
14.	27.899	0.608	2.183	None	None	0,608	2,183
15.	17,468	0.353	2.020	0,031	0,180	0,384	2,200
16.	16.679	0,610	3,660	0,023	0,140	0,634	3,799
17.	18.119	0,065	3,610	0,065	0.360	0,719	3,970
18.	24,161	0,558	2,310	0.486	2,010	1,044	4,320
19.	24.392	0.573	2.350	0,498	2,040	1.071	4,390

* Refers to treatments in Table 7. Compare it for firming and
brine-cracking of cherries.

Table 14.

Interrelationships of pectic substances in the differently
treated brined cherries after about one year storage at room
temperature (70° F.) and their correlation to firmness and
brine-cracking.

(Fresh weight basis)

	RATIOS		
Treatments*	Total pectin to Protopectin	Total pectin to Soluble pectin	Protopectin to Soluble pectin
1.	1.174	6.743	5.743
2.	1.068	15.698	14.698
3.	1.218	5.579	4.579
4.	1.470	3.126	2.126
5.	1.683	2.465	1.465
6.	1.228	5.382	4.382
7.	1.472	3.121	2.121
8.	1.079	13.746	12.746
9.	1.872	2.146	1.146
10.	1.000	-	-
11.	1.363	3.757	2.757
12.	-	-	-
13.	-	-	-
14.	1.000	-	-
15.	1.090	12.081	11.081
16.	1.039	26.963	25.963
17.	1.100	11.000	10.000
18.	1.871	2.149	1.149
19.	1.867	2.153	1.153

* Refers to treatments in Table 7. Compare it for firming
and brine-cracking of cherries.

Table 15.

Effect of different treatments on the permeability as shown by the uptake of mineral elements by the cherries after one year of storage at room temperature (70° F.).

Treat-ments*	CALCIUM (gm. %)		MAGNESIUM (mgm. %)		ALUMINUM (mgm. %)	
	Fresh wt. basis	Dry wt. basis	Fresh wt. basis	Dry wt. basis	Fresh wt. basis	Dry wt. basis
1.	0.134	0.743	1.920	10.00	0.349	1.836
2.	-	-	-	-	-	-
3.	-	-	-	-	-	-
4.	0.162	1.425	-	-	-	-
5.	0.158	1.238	-	-	-	-
6.	0.170	1.489	-	-	-	-
7.	0.166	1.206	-	-	-	-
8.	0.160	1.484	-	-	-	-
9.	0.162	1.510	-	-	-	-
10.	0.154	1.325	-	-	-	-
11.	0.156	1.368	-	-	-	-
12.	-	-	-	-	-	-
13.	-	-	-	-	-	-
14.	-	-	24.256	220.00	-	-
15.	-	-	29.083	250.00	-	-
16.	-	-	31.016	270.00	-	-
17.	-	-	31.701	273.00	-	-
18.	-	-	-	-	1.631	12.270
19.	-	-	-	-	2.843	21.453

* Refers to treatments in Table 7. Compare it for firming and brine-cracking of cherries.