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*Procedure for  
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Sodium Chlorite*

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# Procedure for Secondary Bleaching Brined Cherries with Sodium Chlorite

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## Bleaching to a uniform white

The problem of non-uniformly bleached as well as incompletely bleached brined cherries is solvable by secondary bleaching with sodium chlorite (Beavers and Payne 1968, 1969). There is neither loss of texture nor development of off flavor when the secondary bleaching is carried out by the methods described in this circular of information.

The use of sodium chlorite for secondary bleaching is protected by U.S. Patent Application S N 700,389 assigned to the Oregon State System of Higher Education. For license to use the process see page 4.

## Factors affecting secondary bleaching

To maintain product quality as well as to conserve sodium chlorite, the major portion of the sulfur dioxide should be removed from the brined cherries prior to secondary bleaching. The quantity of sodium chlorite consumed as effected by the sulfur dioxide content in the cherries is shown in Figure 1 which depicts the bleaching curve obtained at a temperature of approximately 70°F. A 0.75 percent sodium chlorite solution at an initial pH of 6.0 was added to the cherries at a ratio of two parts solution to one part of fruit on a weight to weight basis; more sodium chlorite was added as required to complete bleaching.

The sulfur dioxide in the cherries at the start of the bleach also affects the rate of bleaching as shown in Figure 2, which gives the bleaching curve at a temperature of approximately 70°F.

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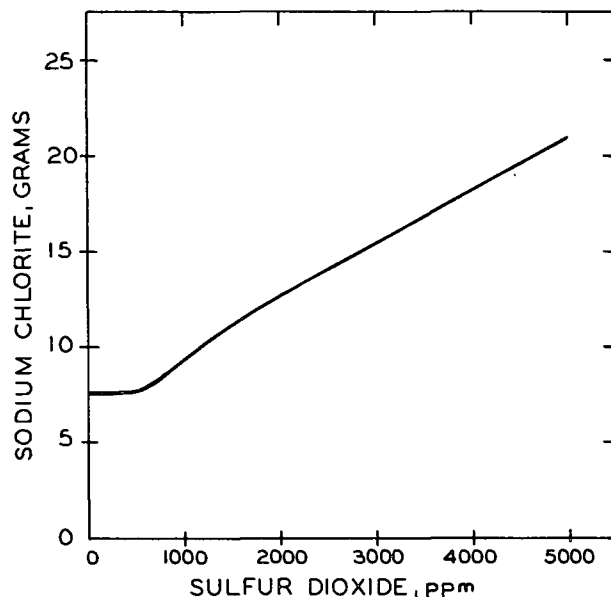


Figure 1. The effect of sulfur dioxide content of 1,000 g of cherries upon the consumption of sodium chlorite during secondary bleaching.

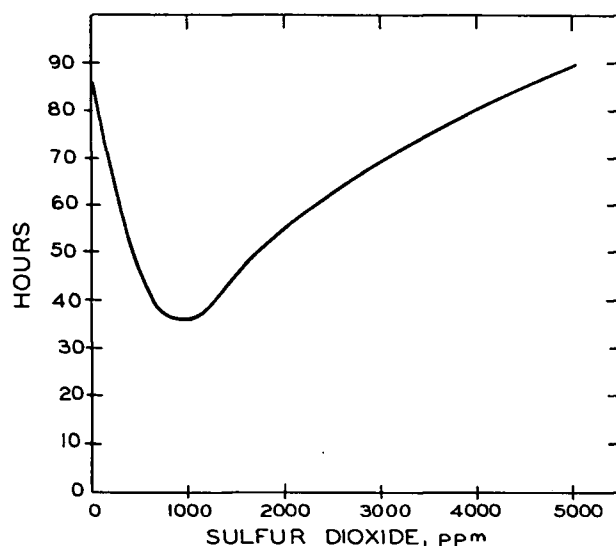


Figure 2. Effect of sulfur dioxide in brined cherries upon the secondary bleaching time.

A 0.75 percent sodium chlorite solution at an initial pH of 6.0 was added to the cherries at a ratio of two parts solution to one part fruit on a weight to weight basis.

Although the maximum rate appears to be in the neighborhood of 900 ppm, the present recommendation is not to have a sulfur dioxide content higher than 700 ppm. Above 700 ppm the control of the bleaching reaction in all parts of the bleaching tank becomes more difficult and more critical.

Lowering the pH or increasing the temperature increases the rate of secondary bleaching as shown in Figure 3, which gives the bleaching curves obtained with cherries leached to a sulfur dioxide content of 100 ppm and placed in a 0.75 percent sodium chlorite solution on a weight to weight basis of two parts solution to one part fruit.

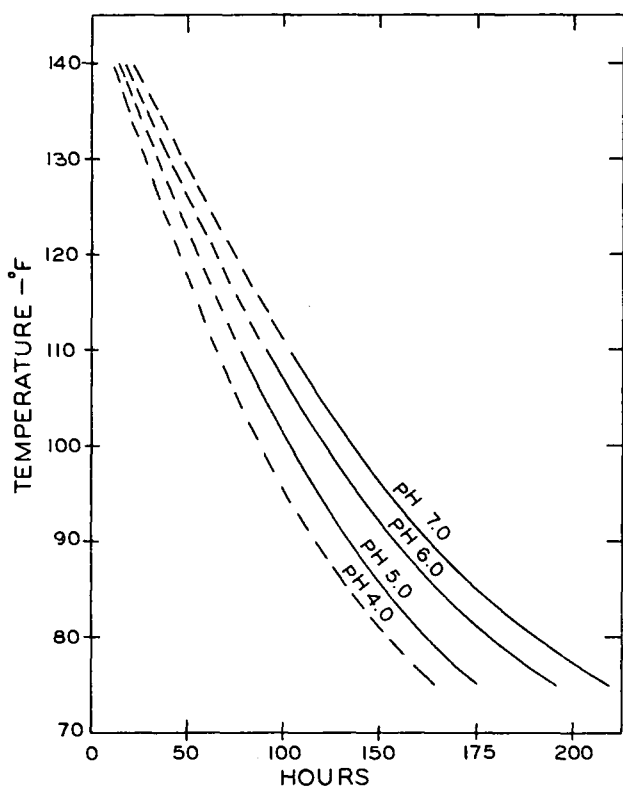


Figure 3. Effect of temperature and initial pH upon secondary bleaching time.

Although lowering the pH increases the rate of secondary bleaching, the nature of the chemical reactions of chlorite changes below a pH of 4.2 and adversely affects the quality of cherries. Hence, the pH should be kept above 4.2 at all times during secondary bleaching.

Increasing the temperature at which the bleaching is conducted increases the rate of bleaching. The temperature should not be above 110°F at the start of the bleach, as gas pockets and

softening of cherries may result. Higher temperatures of up to a maximum of 140°F can be used to speed completion of the bleaching action (when bleaching is partially completed and tests on a small batch indicate gas pocket formation is no longer a problem).

Secondary bleaching of unpitted cherries is not recommended. If practically all of the sulfur dioxide is not removed from the cherries, serious gas pocketing and softening occur. Because of the prolonged time required to leach the cherries, it is difficult to remove practically all of the sulfur dioxide without some fermentation occurring. Acetaldehyde, which results from fermentation (Amerine 1967), can cause the secondary bleaching reaction to go out of control. In any event the faster method (Method #2) of secondary bleaching described below should not be used on unpitted cherries.

### Two methods recommended for commercial use

#### *Method #1*

The first method for secondary bleaching of brined cherries is based upon leaching cherries to less than 200 ppm sulfur dioxide, then transferring the cherries to a solution of sodium chlorite having a pH of 5.0 and bleaching to completion at a pH above 4.2.

#### *Method #2*

The second method is designed for faster bleaching and should be considered when operating temperatures are approximately 55°F or below, and a month or longer may be required to complete the secondary bleaching by Method #1. In the second method, the brined cherries are leached to 500 to 700 ppm SO<sub>2</sub> and then bleached with a sodium chlorite solution having an initial pH of 6.0 to 11.0. The pH is not allowed to drop below 4.2 during the bleaching operation.

### Sodium chlorite

Commercial food grade sodium chlorite contains approximately 82 percent active ingredients, and the directions in this circular are based on an active sodium chlorite content of 82 percent. A 0.75 percent solution of this grade of sodium chlorite obtained domestically has a pH of 11.0; sodium chlorite obtained from foreign sources has a pH of about 7.0. Hence, adjustments for pH prior to secondary bleaching depend on the source of sodium chlorite as described in the directions that follow.

The test for sodium chlorite in the secondary bleaching solution is based upon its oxidizing potassium iodide to free iodine, then determining the free iodine with sodium thiosulfate. (Haller and Listek 1948—see Appendix III.)

## Secondary Bleaching Method No. 1

1. Place 1,000 lbs.\* of brined, pitted cherries into a wooden or plastic-lined tank and leach with running water until the SO<sub>2</sub> in the cherries is 100-200 ppm. For a description of the method for determining SO<sub>2</sub>, see Appendix I.

Leaching takes one to two days. The time can be shortened by use of hot water. Thus, an alternative method is to place cherries in a steam-jacketed kettle, cover with water, bring to a boil and continue boiling for 10 minutes, then drain. This procedure is repeated with 10-minute leaches with boiling water, until the SO<sub>2</sub> in the cherries is less than 200 ppm.

2. In a separate container run in 2,000 lbs. of water (240 gallons). Mix in 15.0 lbs. of sodium chlorite and stir until completely dissolved. Continue the mixing and add as a buffering agent 200 ml glacial acetic acid if using domestic sodium chlorite or 300 g sodium acetate if using imported sodium chlorite at pH 7.0. The pH after addition of acid or sodium acetate should be 5.0.

The secondary bleaching is carried out using two parts by weight of this 0.75 percent sodium chlorite solution to one part by weight of cherries. In many instances less sodium chlorite could be used, but the minimum amount of sodium chlorite necessary for bleaching will have to be determined by experimentation (use same volume of water but smaller quantity of sodium chlorite). In any event, as the bleaching nears completion, only a small amount of sodium chlorite, as little as 0.03 percent, will complete the bleaching.

Do not allow rubber to come in contact with the sodium chlorite; use neoprene gloves and aprons, and protect eyes with goggles. Wood barrels or tanks may be used; pumps, piping and tubes should be of plastic.

3. Drain water from leached cherries and add the freshly prepared sodium chlorite solution. Cover with 8 mil polyethylene film and make a tight seal with water on top of the plastic film.
4. Recirculate the sodium chlorite solution continuously or at least once every four hours to prevent stratification of bleaching action. Solu-

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\* For other amounts of cherries, increase or decrease the amount of sodium chlorite solution prepared in step 2 proportionately. For a barrel-size batch use 150 lbs. of cherries and a factor of 3/20 on the other ingredients specified. Since the work involved in checking and controlling the secondary bleaching process is the same for each container, it is advisable to have one large tank rather than a number of barrels or other small containers.

tion inlet and exit points must be located so as to secure displacement flow of solution from *all* parts of container.

Recirculation is necessary to secure uniformity of solution composition *and* temperature; otherwise dead spots and hot spots may develop and not only will the bleaching action be non-uniform, but may get out of control in parts of the container. Thus, if the pH in one section of the container falls below 4.2, the chlorite undergoes a different type of chemical reaction and free gaseous chlorine dioxide will be evolved. (Chlorine dioxide is irritating and harmful to the respiratory tract and can be fatal.)

There should be no problem with the pH dropping below 4.2 if the leaching at step 1 has been properly conducted, the sodium chlorite solution is buffered as directed in step 2, and the solution is recirculated during the bleaching operation. If necessary, dilute caustic (sodium hydroxide) should be added to keep pH above 4.2 at all times. Don't adjust pH unless necessary, as adding caustic when pH is below 5.0 will result in permanent loss of some sodium chlorite.

5. Test for bleach completion after 5 to 10 days, depending on temperature. When bleaching is completed the cherries will be completely white and will not develop a brown discoloration when heated. (Heat reversion color—see Appendix II for test method.)

Some processors using secondary bleaching believe that a little bit of heat reversion color is desirable for darkening the red shade of color obtained on dyeing; others believe that absolute white color, which is easier to duplicate, is essential for securing a brilliant red.

6. Leach secondary bleached cherries in running water for 1 to 2 days to remove any remaining sodium chlorite.
7. To assure a desirable firm texture in the cherries, they should be returned to a 1 percent SO<sub>2</sub>—lime brine with a pH of 3.3 buffered by addition of sodium acetate (0.05 to 0.1 percent by weight of the brine). After 2 weeks the cherries are ready for leaching and further processing into Maraschino cherries.

If firmer fruit is desired, 1 to 2 percent calcium chloride may be added in step #2 above, provided that the pH is adjusted back to 5.0 after the calcium chloride addition.

## Secondary Bleaching Method No. 2

1. Same as in Method No. 1 except that leaching should be stopped when the  $\text{SO}_2$  is about 500 to 700 ppm. When cold running water is used, the leaching should be completed in 15 to 24 hours.
2. Prepare the sodium chlorite solution for 1,000 lbs. of pitted cherries by mixing 15.0 lbs. of sodium chlorite in 2,000 lbs. (240 gallons) of water. Adjust pH to 11.0 with dilute caustic (sodium hydroxide) if necessary and then add 300 g of sodium acetate as a buffer.

A more rapid bleach can be obtained by adjusting the pH of the sodium chlorite solution in the range of 6.0 to 9.0 before addition of 300 g of sodium acetate buffer (the lower the initial pH the faster the bleach). However, this sodium chlorite solution with the pH in this lower range should not be used unless the secondary bleaching action is constantly monitored and controlled. The pH must not be allowed to drop below 4.2; otherwise, the process may get out of control. The bleaching solution must be continuously recirculated to all parts of the tank to prevent localized hot spots from developing, as the process then can get out of control before it becomes noticeable by routine monitoring.

In addition to securing a faster bleach, the use of lower initial pH sodium chlorite solution results in less sodium chlorite being consumed in the process.

3. Same as in Method No. 1. Temperature of the bleaching solution must be kept below 70°F, otherwise pocketing and softening will develop in the cherries.
4. Same as in Method No. 1 except that continuous recirculation is recommended because of the faster bleaching action.
- 5, 6, and 7. Same as in Method No. 1.

## Patent License for Secondary Bleaching with Chlorite

The use of sodium chlorite for secondary bleaching of brined cherries as well as other fruits and vegetables is protected by U.S. Patent Application S N 700,389 assigned to the Oregon State System of Higher Education. (Patent protection is also pending in 17 foreign countries.)

For licensing information write the Vice-President and Director of Patent Programs, Research Corporation, 405 Lexington Avenue, New York, N.Y. 10017, authorized agent for the Oregon State System of Higher Education.

## APPENDIX I

### Determining $\text{SO}_2$ in Brined Cherries

From a chemist's point of view, brined leached cherries are approximately 3 percent cellulosic and pectic material and 97 percent water containing traces of water soluble constituents. To determine the sulfur dioxide in the cherries, take a sample of about 25 cherries (approximately 100 to 150 g), grind to a pulp in a blender, and filter the pulp on No. 4 filter paper. (Do not wash pulp residue on filter paper.)

Pipette 5 ml of the filtrate into a 250 ml Erlenmeyer flask containing approximately 100 ml distilled water. Add 1 ml of starch solution and 5 drops of 20 percent sulfuric acid. Titrate with standardized 0.156 N iodine solution until a blue color persists for 30 seconds (the first blue color that persists for 30 seconds). Multiply the ml iodine required by 1,000 to obtain parts per million free sulfur dioxide.

This method is modified from that of the Association of Official Agricultural Chemists (AOAC, 1965) for determination of free sulfur dioxide (Payne and others 1969). The sample solution is acidified to liberate sulfurous acid from its soluble salt forms and to prevent release of organic-bound sulfur dioxide. The sulfurous acid is oxidized with standardized iodine. The starch indicator, which is colorless in the presence of sulfur dioxide, gives a distinct blue-black endpoint with a trace of excess iodine.

### Required Reagents

*Iodine stock solution (1.56 N).* Dissolve accurately weighed quantities of 198.4 g resublimed iodine (ACS) and 310.0 g potassium iodide (C.P.) in a liter volumetric flask containing 250 ml distilled water. When the iodine is completely dissolved, make to volume with distilled water. Store all iodine solutions in an amber glass container away from light. Iodine is not stable in the presence of light, decomposing to hydriodic acid. High temperature storage will cause some volatilization of iodine. Therefore, it is necessary to restandardize iodine solutions frequently.

*Standard (0.1 N) sodium thiosulfate solution.* Dissolve exactly 24.82 g of fresh sodium thiosulfate pentahydrate (ACS) and make to 1 liter with distilled water. This solution is used to standardize the iodine solution.

*Starch indicator solution.* Dissolve 1 g of water-soluble potato starch in 100 ml distilled water, heat to boiling, and cool. To retard mold growth after preparation of the solution, add a few drops of mercury and shake vigorously. Discard solution if mold growth appears.

## APPENDIX II

### Determining Completion of Secondary Bleaching

The test for completion of bleaching consists of heating a sample of pulped cherries in sirup. When bleaching is complete the heated pulp will remain white and not show any brown discoloration (heat reversion color).

A representative sample of 150 g is pulped in a blender for two minutes, then rinsed with 4,000 ml of water on a milk filter pad or other coarse, non-corrosive filtering medium. The purpose of rinsing is to remove any sodium chlorite remaining in the cherries, which during the subsequent heating, would continue bleaching at an accelerated rate and result in a false test. The pulp remaining on the filter is removed and blended again in a blender for two minutes, and again rinsed with 4,000 ml of water on a coarse filter pad.

The washed pulp is removed from the filter and returned to blender with 25 percent acidified sucrose solution to give a total volume of 150 ml. After blending in blender for two minutes, a 25 ml portion is placed in a 25 X 200 mm test tube and heated for 15 minutes in boiling water. Development of a brown color indicates incomplete bleaching.

When the color of the heated fruit pulp reaches that of a predetermined white standard, the secondary bleaching is considered completed and the cherries are ready for the next step of leaching.

#### Required Reagents

*Acidified sucrose solution* (25 percent). Add 250 g of sucrose (refined cane or beet sugar), 3.0 g citric acid, and 1.0 g sodium benzoate to distilled water and make up to 1 liter. Then adjust to pH 5.0 with 1 N sodium hydroxide.

*Sodium hydroxide* (1 N Unstandardized). Add 40 g of sodium hydroxide to distilled water and make up to 1 liter.

## APPENDIX III

### Determining Sodium Chlorite ( $\text{NaClO}_2$ )

Sodium chlorite in the bleaching solution is determined by the modified method of Haller and Listek (1948). Potassium iodide is added to the solution and the chlorite present oxidizes the iodide to free iodine, which is then determined by titration with sodium thiosulfate.

A 5 ml sample of the bleaching solution is measured into a 250 ml flask containing 100 ml of distilled water. Fifteen ml of 1 N potassium iodide and 5 ml 6 N sulfuric acid are added, and the solution titrated with 0.1 N sodium thiosulfate solution to a colorless endpoint (starch indicator solution

*Sulfuric acid solution* (20 percent volume to volume). Add 20 ml of concentrated sulfuric acid (C.P.) to 80 ml of distilled water.

*Standard iodine solution* (0.156 N). Pipette 100 ml of iodine stock solution (1.56 N) into a 1-liter volumetric flask and dilute to volume with distilled water. Standardize before using.

*Standardization of iodine solution.* Transfer 10 ml of standard sodium thiosulfate to a flask containing 100 ml distilled water. Add 1 ml of starch solution and 5 drops of 20 percent sulfuric acid. Titrate with the iodine to be standardized to the first permanent blue endpoint. The normality of the iodine solution is calculated as follows:

$$\text{Normality of iodine} = \frac{10 \text{ ml thiosulfate} \times 0.1 \text{ N}}{\text{ml iodine required}}$$

If the normality is high or low, add 1 ml distilled water or 0.65 ml of iodine stock solution, respectively, for each 0.001 N difference and restandardize with sodium thiosulfate.

*Sulfur dioxide equivalent (SDE).* Defined as parts per million sulfur dioxide per ml of iodine solution used. Given the normality of iodine and volume of sample solution, the SDE can be calculated:

$$\text{SDE} = \frac{\text{Normality of iodine solution} \times 32,000}{\text{ml of sample solution}}$$

In the interest of accuracy and/or conservation of iodine solution, it is often necessary to use less concentrated iodine solutions or larger sample volumes. The SDE for several common sample volumes and normalities are given below:

Normality	Brine sample size (ml)	SDE
0.156	5	1,000
0.156	10	500
0.100	5	640
0.100	10	320
0.050	10	160
0.001	5	64

The concentration of sulfur dioxide in parts per million can be obtained by multiplying the ml of iodine required in titration by the SDE for the particular normality and sample size used.

(1 percent) is added just preceding complete destruction of iodine). Designate this thiosulfate titer as titration B. The percent  $\text{NaClO}_2 = B (0.04523)$ .

Because of the formation of some chlorine dioxide when the solution is acidified with sulfuric acid, the value obtained may be as much as 1 percent too high; that is, the true value may only be approximately 0.99 of the value determined by this titration. If a more accurate value is required, take another 5 ml aliquot of bleaching solution and add to a flask containing 100 ml distilled water. The solution is made alkaline with 15 ml 1 N sodium hydroxide, stoppered, and allowed to stand undisturbed for 30 minutes. Fifteen ml of 1 N potassium iodide is added, the solution acidified with 10 ml of 6 N sulfuric acid, and titrated to a colorless endpoint with 0.1 N sodium thiosulfate. Designate this thiosulfate titer as titration A. Designate C as  $(B \text{ titer} - A \text{ titer}) \frac{5}{3}$ . Percent  $\text{NaClO}_2 = (B - C) 0.04523$ .

#### *Required Reagents*

*Potassium Iodide Solution (1 N)*. Dissolve exactly 166.0 g of potassium iodide and make up to 1 liter with distilled water.

*Sodium Thiosulfate Solution (0.1 N)*. Dissolve exactly 24.82 g of fresh sodium thiosulfate pentahydrate (ACS) and make to 1 liter with distilled water.

*Starch Indicator Solution*. Dissolve 1 g of water-soluble potato starch in 100 ml distilled water, heat to boiling, and cool. To retard mold growth, after preparation of solution add a few drops of mercury and shake vigorously. Discard solution if mold growth appears.

*Sulfuric Acid Solution (6 N Unstandardized)*. Add 166.0 ml of concentrated sulfuric acid to distilled water and make up to 1 liter.

*Sodium Hydroxide (1 N Unstandardized)*. Add 40.0 g of sodium hydroxide to distilled water and make up to 1 liter.

#### ACKNOWLEDGMENTS

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