FACTORS WHICH PRODUCE BLEACHING OF PICKLES

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Leon Eisenstat

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THESIS

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Leon Eisenstat

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F. W. Fabian
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FACTORS WHICH PRODUCE BLEACHING OF PICKLES

By

Leon Eisenstat

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INTRODUCTION

The bleaching of pickles has become an important problem in the pickle industry. It is a common observation that pickles floating on top of an uncovered salting tank will, in time, become completely blanched. Such bleached pickles are discarded, and the resultant loss to the industry may be great. In addition to the bleaching of salt stock pickles, bleaching occurs even more frequently after desalting, either before the pickles are bottled, or after bottling. The pickles may be completely bleached, or bleached areas may appear; commonly on one end, the blossom end, which becomes colorless or a light tan. No batch of pickles seems to be assured of immunity from attacks of whitening. Bleaching may be found not only in sour, sweet, and dill pickles, but even in fresh cucumber pickles and in genuine dills.

Attempts to cope with the problem of bleaching have taken various turns, depending on the plant involved. Salting stations and pickle packers, who are aware of the destructive effects of sunlight, keep their pickle vats or barrels covered with canvas while they are being filled or emptied. That is the extent of the preventive measures used by most plants. Turmeric is added to cover up the color loss, and its use is standard practice for processed pickles. Turmeric definitely yellows the pickle, and its use results in a more natural looking color, although pale areas still remain pale. Other measures used to restore the color include pasteurization of the pickles, use of certified food colors, and the addition of copper to the jar. Except for pasteurizing, these methods attempt to darken the faded areas on the pickle or to color the liquor in order to make the bleached areas less conspicuous. None of these measures, however, restore the green color completely; in most cases, they serve only to make the green portions greener and to accentuate the contrast between the bleached and unbleached portions of the pickle.

LITERATURE REVIEW

In spite of the wealth of information already published on pickles and pickle products, the literature concerning bleaching of pickles is virtually non-existant.

Fabian, Bryan, and Etchells (1932) found that the presence of iron salts caused the blackening of pickles and pickle brine. Blackening occurred only when the brines were alkaline or practically neutral.

Fabian and Nienhuis (1934) discovered that an organism to which the name Bacillus nigrificans was given also caused blackening in pickle brine.

Carpenter (1933) found that the color, as well as the aroma and flavor, of apple and kraut juices was definitely affected by light. Green light was found to be best for preserving the original qualities of the juices.

Mayer (1939) stated that the gradual bleaching of carotene occurs as the crystals absorb oxygen from the air.

Smith (1949) discussed the greening of plants and the inhibition of greening at high and low temperatures.

Strain (1949) noted that strong oxidizing agents, such as ferric ions, and active reducing agents, such as zinc powder, convert chlorophyll, the pigment responsible for the green color of pickles, into labile, colorless products.

Bauerfeind (1950) found crystalline l-ascorbic acid useful in retarding color and flavor changes in foods caused by oxidative activity and by the action of enzymes.

Pivnick (1950), who investigated, for Dr. F. W. Fabian, extensive bleaching encountered in a commercial pickle plant during the manufacture of processed dill pickles, found that bleaching, on the batches of pickles investigated, started in the center of the pickles and increased in extent until the whole pickle, inside and out, was bleached.

EXPERIMENTAL PROCEDURE

Commercially, sweet pickles and processed dill pickles are produced in the greatest volume. Of these, dills are whitened with much greater frequency than sweets, which, by comparison, are bleached only rarely. For this reason, and also because of the magnitude of the problem, experimental work was confined to dill pickles and to their precedent salt stock.

The source of all the pickles subjected to the numerous tests which follow was salt stock obtained from the H. W. Madison Co., a commercial salting station in Mason, Michigan. The pickles obtained were in a brine of 60° salometer (16% salt). The sizes used ranged from 1,200 to 4,500, depending on availability. For more than half the tests, pint Mason jars were used. Two pickles were added to each jar and the appropriate liquor poured over them, so that the pickles were completely immersed in liquid; then the cap was screwed down tightly. The tests which employed jars were nearly always performed in duplicate. After completion of the test, one jar was placed on a laboratory shelf exposed to light, and the other was packed in a carton, the openings of which were covered with brown wrapping paper and put away in the darkness of a laboratory closet. Thus, for most tests where jars were employed, two jars were used, one of which was kept in the light on completion of the test, and the other was kept in the dark until both jars were ready for examination.

When desalted pickles were used, the salt stock was desalted by flowing water for at least twenty-four hours. The pickles were then tested for salt content by titrating with standard silver nitrate solution, using dichlorofluorescein indicator. In order to standardize all tests, the desalted pickles were weighed, and appropriate amounts of the following ingredients were added, so that when the pickles came to equilibrium with the brine, the components would be present in the concentrations below:

1. Alum, 0.2% $Al_2(SO_4)_3 \cdot 18H_2O$, so as to yield 0.1% $Al_2(SO_4)_3$,
2. Vinegar, to give a dilution of eight grains. The stock supply was either 120 grains or 159 grains.
3. Salt, 3.8% final dilution, allowances being made for the residual salt in the pickles,
4. Spices, sufficient spice emulsion being used to give an actual 1-3,000 dilution of spice oils. The emulsion was prepared from the materials in these proportions:

Emulsion gum..................	454.5 gm.
Tween 20	60 gm.
Oil of dill...................	767 gm.
Oleoresin of black pepper.....	767 gm.
Oil of mustard................	284 gm.
Oil of garlic.................	trace
Water.........................	1,909.5 gm.

In this emulsion, the spice oils comprise three-sevenths by weight of the emulsion (or, conversely, the complete emulsion is 7/3 the weight of the spice oil ingredients alone).

In the tests which follow, in order to simplify the analysis of the large mass of data, the effects on the two pickles in each jar were averaged, and the outcome presented as a single result. Where jars were not used, the effect on each pickle has been listed as a separate result.

The results are recorded according to the amount of bleaching which occurred. The amount of bleaching was graded as follows:

-	= None						
±	= Doubtful bleaching						
B	= Bleaching just beginning; less than 1/8 pickle						
⊢	= 1/8,	about	13%,	of	surface	exposed	bleached
+	= 1/4,	"	25%,	"	"	"	"
+⊢	= 1/3,	"	33%,	"	"	"	"
++	= 1/2,	"	50%,	"	"	"	"
++⊢	= 2/3,	"	67%,	"	"	"	"
+++	= 3/4,	"	75%,	"	"	"	"
++++	= Complete, 100%						

FACTORS TESTED AND RESULTS

Effect of Light

1. Diffused Light

In order to determine the influence of diffused light on pickles, the following experiments were performed: Four sets of salt stock pickles were placed in glass jars, and after covering the pickles with their original brine, the jars were capped. Each of the jars was treated differently: one was left standing on the laboratory shelf; another was kept in the dark, and the other two were sealed with paper to exclude light. A second group of desalted pickles was given the same treatment as the salt stock pickles. A third group of desalted pickles was placed in jars without any brine, and a fourth group was placed on waxed paper after desalting. Except for the jars in the dark, the pickles were all left exposed to the diffused light in the laboratory for two weeks. The results are given in Table 1.

Table 1. - Bleaching effect of diffused light on pickles

	Salt Stock Pickles + brine in jar	Desalted Pickles + dill brine in jar	Desalted Pickles in empty jar	Desalted Pickles on wax paper
Jar kept in light	-	+	+	+
Jar kept in dark	-	-	+	-
Jar sealed with white paper	-	-		
Jar sealed with black paper	-	+		

2. Direct sunlight

Desalted pickles were placed in glass pans above a layer of dill brine, so that all but the bottom surface of the pickle was completely exposed. They were then exposed outside the laboratory to direct sunlight.

Table 2. - Bleaching effect of direct sunlight on desalted pickles

	Time of Exposure			
	3 3/4 hours	4 1/2 hours	7 hours	8 1/2 hours
Pickles exposed	+	+++	+++	++++
	+	+++	++++	++++
	++	++++	++++	++++
	++	++++	++++	++++
Controls -- not exposed	-	-	-	-
	-	-	-	-
	-	-	-	-
	-	-	-	-

3. Infrared radiation

Salt stock pickles and desalted pickles were given a large number of different treatments with infrared rays. The rays were obtained by the use of a General Electric Company lamp, 250 watts, reflector type. This was securely clamped to a ringstand. On the base of the ringstand was placed a large mortar, into which the pickles, or brine, or jars to be exposed, were placed. The lamp was fixed at a constant distance of eight inches from the bottom to the inside of the mortar. The distance was not changed to allow for differences in pickle sizes. A General Electric timeclock timed the period of exposure. (The exposure times are found in column 1 of Tables 3 and 4). When the exposures were completed, the pickles were returned to their jars, and observations made on the effect of the treatment a week-and-a-half later. The results are found in Tables 3 and 4.

Table 3. - Bleaching effect of infrared rays on desalted pickles

	Water Added After Exposure		Dill Brine Added After Exposure		Pickles & Dill Brine Exposed Together		Dill Brine Exposed, then Pickles Added		Jars Exposed--Pickles & Brine Inside		Controls--No Exposure	
Time of Exposure	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark
1 min.			++	++					++	+	-	-
2 min.			+	++	±	∓	+	-	++	++	±	-
4 min. (2 min. 2 days)			++	+	++	±						
5 min.	±	+	++	±	+	±	-	+	±	-		
6 min. (2 min. 3 days)			++	++	++	++			++	-		
10 min.	++	+	+	+	++ +	∓	+	±	-	+		
10 min. (5 min. 2 days)			+	++	++ ++	- ++			+ +	++ +		
15 min. (5 min. 3 days)			+++	+					++	+		
20 min.	++	+	+++	+	+	+	+	-	+	+		
20 min. (10 min. 2 days)					+	++						
30 min.			++	++	++ ++	∓ +	-	±	+	+		
40 min. (20 min. 2 days)					++	++			+ ++	+++ ++		
1 hour			++	++					+	++		
1 hour (30 min. 2 days)			++	++					B	++		
$1\frac{1}{4}$ hours (15 min. 5 days)			++	++								
2 hours (30 min. 4 days)			++	+++	+++	++			+	++		
3 hours (30 min. 6 days)			++	+++	+++	+++						

Table 4. - Bleaching effect of infrared rays on salt stock pickles

	Pickles Exposed, then Desalted		Pickles Exposed Returned to Brine Not Desalted		Pickles & Brine Exposed Together. Not Desalted		Pickles & Brine Exposed Together Pickles Desalted		Only Brine Exposed. Pickles Desalted after Brine Exposed		Pickles Completely Covered by Brine Desalted after Exposure		Pickles Exposed, then put in Empty Jar	
Time of Exposure	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark
2 min.	+	-	-	-										
5 min.	++⊢	⊢	-	-										
10 min.	⊢	-	-	-										
20 min.	⊢	⊢	-	⊢										
30 min.	+⊢	+⊢												
30 min. (10 min. 3 days)	+	+												
40 min. (20 min. 2 days)	+⊢	⊢												
1 hour	+⊢	+												
1 hour (30 min. 2 days)	+⊢	+⊢			-	⊢	B	-						
1 hour (20 min. 3 days)	+	+⊢												
$1\frac{1}{2}$ hours (30 min. 3 days)	+⊢	⊢												
2 hours													+	⊢
2 hours (30 min. 4 days)	⊢	+					⊢	±	⊢	B				
3 hours (30 min. 6 days)	+	+					+	+			-	-		
Control Not Exp.	-	-	-	-										

4. Ultraviolet Rays

Whatever the source of ultraviolet irradiation in the laboratory, it is recognized that the effect will not be a duplication of conditions as they exist in nature. Pickles floating on the surface of tanks are obviously exposed to ultraviolet rays. In these experiments, the ultraviolet source was, of course, different from that which pickles would normally encounter. It was a 15 watt G. E. sterilizing bulb. This is known to transmit most of its rays around 2537 Å. It should be made clear, therefore, that the ultraviolet band used covered mainly the bactericidal range, the portion between 2100 and 3287 Angstrom units. That this range was not the limits of the emission was evident from the fact that the light could be seen. Part of the visible spectrum, then, must have been present also. The bulb used was placed about two inches from the pickles to be tested. The pickles, or brine, or pickles and brine, were placed on a pan directly below the bulb. The shorter of the two pickles in each jar was wiped before exposure to determine whether any difference would result in exposures of wet and dry pickles. As with infrared treatment, the pickles were put back in their jars after exposures. The results are given in Tables 5 and 6. Column 1 in each table lists the times of exposure to the ultraviolet light, and the other columns, the bleaching action, if any, on the pickles. Observations of the effect of the irradiation were made a week after treatment.

Table 5. - Bleaching effect of ultraviolet rays on desalted pickles

	Water Added After Exposure		Dill Brine Added After Exposure		Pickles & Dill Brine Exposed Together		Dill Brine Exposed. Pickles Added After Exposure		Pickles Exposed, Then Put in Empty Jar.		Controls- No Exposure	
Time of Exposure	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark
1 min.			+	⊦							-	⊦
2 min.			+	-							⊦	⊦
4 min. (2 min. 2 days)			+	±								
5 min.	⊦	⊦	+	B	⊦	-	+⊦	±				
10 min.			⊦	B	+⊦	⊦	⊦	⊦				
10 min. (5 min. 2 days)			+	-								
15 min. (5 min. 3 days)			+	⊦								
20 min.			⊦	-	-	±						
20 min. (10 min. 2 days)			+	⊦								
20 min. (5 min. 4 days)			+	⊦								
30 min.			±	⊦	+	⊦						
40 min. (20 min. 2 days)			⊦	⊦	⊦	⊦						
1 hour			+	⊦	⊦	-						
1 hour (30 min. 2 days)			⊦	B	+⊦	+						
2 hours (30 min. 4 days)			+	⊦	++++	+			⊦ 2 hrs. Continuous Exp.	±		
3 hours (30 min. 6 days)			++	+⊦			⊦	-				

Table 6. - Bleaching effect of ultraviolet rays on salt stock pickles

	Pickles Exposed, then Desalted		Pickles Exposed, Not Desalted. Returned to Brine		Pickles & Brine Exposed Together. Pickles Desalted		Pickles Exposed, then put in Empty Jar		Controls--Not Exposed	
Time of Exposure	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark
5 min.	+	+	-	-					-	-
10 min.	+	+	-	+					-	-
20 min.	+	±			+	+				
20 min. (10 min. 2 days)	+	+								
30 min.	++	B			++	+				
40 min. (20 min. 2 days)	+	+								
1 hour	B	+	++	+	++	+				
1 hour (30 min. 2 days)	+	+			+	+				
2 hours							+	±		
2 hours (30 min. 4 days)	+	+			+	+				
3 hours (30 min. 6 days)	+	+			+	+				

Discussion of Results

From Table 1, it may be seen that salt stock pickles in their original brine did not whiten either when exposed to diffused light or kept in the dark. Desalted pickles, however, were bleached in the light, and in two of four cases when light was excluded.

By reference to Table 2, it may be seen, as is generally known, that sunlight is a rapid and powerful bleaching agent for pickles. Every pickle exposed to the sun whitened, whether the time of exposure was 3 3/4 hours, or longer. In as little as 4 1/2 hours, some of the pickles tested were completely bleached.

This bleaching effect of direct sunlight serves to confirm a fact long known by the pickle packer. White pickles floating on top of a salting tank--a common sight--attest to the effectiveness of the sun's rays in eliminating pickle color. The information obtained, then, from Table 2 is not new. But these experiments aimed to go a step further and to determine whether the infrared or ultraviolet rays in the sun's spectrum were the destroyers of pickle color. The tests on infrared rays were carried out first.

One hundred fifty-three jars of pickles were exposed in various ways to infrared radiation. Of these, 48 were jars containing salt stock pickles, and 105 were jars which contained desalted pickles. Of the total, only 24 jars were definitely negative, and showed not the slightest indication of color loss. Of the 24 negative jars, four had not been exposed at all; only the brine had been subjected to infrared radiation. On the other hand, 115 jars showed clear, unmistakable bleaching.

Reference to Table 3 indicates clearly that desalted pickles were very readily bleached when exposed to infrared radiation. Eighty-six jars were clearly positive, one showed bleaching just beginning (B in column 10), seven were doubtful (±), and only 11 jars were definitely negative. Of the 11 negatives, in four jars, only the dill brine was exposed, and in three jars, the infrared lamp had been directed at the pickles through the glass jars. One would naturally suppose that if infrared rays had bleaching properties and could pass through glass jars, they would need longer exposure periods to penetrate both the glass and the brine. It is not surprising, then, that three negative results occurred when jars were exposed for only five, six, or ten minutes. When exposure times were longer than ten minutes, some bleaching was apparent in every jar. Yet, paradoxically, exposure periods shorter than five minutes (one and two minutes) resulted in marked bleaching in all of the four jars tested. The amount of bleaching was large, in most cases. More than a fourth of the exposed pickle surface was bleached in 52 of the jars of desalted pickles tested.

It will be seen, then, that the bleaching effect of infrared radiation was definite and unmistakable. In a few cases, the color loss became apparent even before the exposures were completed. As already mentioned, ordinary glass pint Mason jars offered no protection from infrared rays; for the pickles in the jars covered with dill brine turned white after the rays had been directed at the closed jars. Even dill brine alone when exposed to infrared rays and then added to pickles, caused the pickles to bleach in about half the experiments undertaken. This last observation must be considered inconclusive, however, since there were about as many negative results as there were positive.

Salt stock pickles did not respond as clearly as did desalted pickles to infrared treatment. In many cases, whitening was not at all apparent until after the pickles had been desalted, placed in jars, and covered with dill brine. Analysis of Table 6 indicates that, of 48 jars tested, 33 showed whitening, two indicated that only a beginning of whitening had been made, and 13 were entirely negative. Of the jars in which no whitening occurred, the brine had completely covered the pickles in two jars, and exposure times were 20 minutes, or less, in nine jars. There were only four jars without any evidence of whitening when exposure times were increased beyond 20 minutes. When pickles were exposed together with their brine, five jars showed whitening, one a slight beginning, and two jars, none. (In this last case about 300 ml. of brine was used, enough to fill a pint jar containing two pickles, but the pickles were not completely covered by the brine, since exposure was in a shallow pan about 15 inches long). When the brine covered the pickles completely, in spite of an exposure time of three hours over a period of six days, the pickles failed to show any color loss. It may be that salt stock brine, at least that which is at 60°

salometer, presents a barrier to the penetration of infrared rays, in contrast to dill brine. It may be observed that salt stock pickles often form a solid cake, or coating, of salt after the water evaporates. This may be a protection against the action of infrared rays; for the pickles so coated were not bleached. The pickles were not wiped dry before exposure, since it was felt that no such practice is carried on in the pickle plant. It will be further noted that there does not seem to be any correlation apparent between the length of exposure and the degree of whitening in the case of salt stock pickles.

The use of ultraviolet irradiation did not produce results as convincing as did the use of infrared rays. Ninety-eight jars, of two pickles each, were exposed to ultraviolet rays for different periods of time. Of these, 40 jars were salt stock pickles, and 58 were desalted pickles. Of the 40 jars of salt stock exposed, 33 jars showed clear evidence of whitening. Of the 58 jars of desalted pickles, in six of them, only the brine was exposed to ultraviolet rays, so that the pickles themselves were exposed in 52 jars. Of the 52 thus exposed, 18 jars showed definite bleaching, while 34 were bleached no more than three of the four jars that served as controls, or else were bleached even less. Thus, of 92 test jars of pickles (plus six jars whose brine was exposed only), irradiated by means of an ultraviolet ray lamp, only 51, little more than half, showed convincing evidence of bleaching.

Reference to Tables 5 and 6 will bring out the fact that salt stock pickles did not seem to bleach any less readily than did desalted pickles when exposed to ultraviolet rays. Whether pickles alone were exposed, or whether the pickles were placed above a layer of brine, the pickles whitened in these experiments with equal ease. None of the pickles bleached very markedly whether the time of exposure was five minutes or three hours. The greatest amount of bleaching that occurred extended over little more than one fourth of the exposed pickle surface.

Experimental work with ultraviolet rays directed upon desalted pickles resulted in the bleaching of 45 jars out of 58 tested. Twenty-four of the jars, however, were bleached to the same extent as three of the four controls, and three of the jars showed only a beginning of whitening. Four jars showed doubtful whitening, while seven of the jars were entirely negative. Thus, only 18 jars out of 58 whitened more than did three of the four controls, 24 whitened as much, and 14 jars, even less, or not at all. Just as with salt stock, there was no appreciable difference in the amount of color loss whether pickles alone were exposed or whether some dill brine, too, was added, as long as the pickles were above the brine. There was no difference, either, whether the pickles were wiped dry before exposure, or not.

Effect of Temperature

Four jars of desalted pickles were examined after a storage period of three weeks at four different temperatures. One jar was kept in a refrigerator at 12° C; another was held in the dark at the temperature of the laboratory, which averaged about 25° C, and the other two were stored in separate incubators. The results are indicated in Table 7.

Table 7. - Bleaching effect of different temperatures on desalted pickles

Temperature of Exposure	Results
12° C.	-
25° C.	-
30° C.	+
37° C.	-

Discussion of Results

Though pickles kept at 30° C. showed a slight amount of whitening, the differences in color between all the pickles at the end of the test were very small. Differences in temperature, therefore, did not seem to have much effect in pickle bleaching.

Effect of Spice Oils

Since spice oils have replaced whole or ground spices in flavoring pickles, the oils were subjected to a number of tests in an attempt to determine whether they were among the factors which produce bleaching. The constituent oils were tested separately and in the spice combination generally employed in dill pickle formulas. The emulsion was prepared so the spice oils would be in a 1-3,000 concentration, as has already been explained. The exposure time for Table 8 was three weeks, and for Table 9, five days.

Table 8. - Bleaching effect of spice oils in combination with other ingredients on desalted pickles

		Dill Oil	Oil of Black Pepper	Oil of Mustard	Oil of Dill, Black Pepper, Mustard, Garlic	Controls--No Spice Oils
Water Only	Jar in Light	⊢	+	-	++	-
	Jar in Dark	⊢	-	-	+	-
Water + Toluene	Jar in Light	++++	++++			
	Jar in Dark	++	++++			
Water + Salt	Jar in Light	±	-	-	⊢	-
	Jar in Dark	-	-	-	-	-
Water + Salt + Toluene	Jar in Light	++++	++			
	Jar in Dark	-	++			
Water + Salt + Alum	Jar in Light	⊢	±	-	+	
	Jar in Dark	⊢	-	-	-	
Water +Salt +Alum +Toluene	Jar in Light		++++			
	Jar in Dark		++			

Table 9. - Bleaching effect of dill oil emulsion in combination with other ingredients on desalted pickles

	Jars Kept in Light		Jars Kept in Dark	
Spices + water	-	-	-	-
Spices + salt	-	-	B	-
Spices + alum	+	-	-	-
Spices + vinegar	B	+	-	-
Spices + salt + alum	-		-	
Spices + salt + vinegar	B		B	
Spices + alum + vinegar	B		-	
Full Dill Formula	-		B	
No Spices -- Water Only	-		-	

Discussion of Results

At the beginning of this experimental work, in the desire to inhibit microbial growth in the pickle jar of extraneous organisms, about 5 ml. of toluene was added to some jars. It soon became evident that toluene itself caused whitening, and its use was subsequently discontinued. Since toluene is a solvent for lipids, and since chlorophyll is soluble in lipid solvents, it seems reasonable to assume that the toluene dissolved out the chlorophyll. Since the spices are used mainly as oils, one might be led to question whether they, too, could dissolve out the chlorophyll.

The combination of all the oils used as an emulsion brought about bleaching when the jars were kept in the light, and in one case, when kept in the dark (next to the last column, Table 8). When this experiment was repeated, however, (Table 9), bleaching did not occur in 22 of the 24 jars tested, whether the jars were kept in the light or in the dark. Dill oil and oil of black pepper, but not oil of mustard, did bring about whitening in some cases, but not in others (Table 8). Where bleaching did occur, the color loss was very slight (except where toluene was used).

Since spice oils are added as an emulsion which combines all the oils, and the oils are not added singly to the dill brine, effects of the individual spice oils would be useful information to determine which component was at fault only if the complete spice emulsion caused whitening. In the experiments reported in Table 9, the spice oils did not bring about a color loss in 22 of the 24 jars tested, as already mentioned. In two jars, a very slight degree of whitening occurred, but alum was used in one jar, and vinegar in the other. As will be seen later, both alum and vinegar brought about some whitening when tested separately.

Effect of Salt Concentration

Salt stock pickles were desalted until the salt content was 1.5%. Then sufficient salt was added so that the jars of pickles plus liquor would contain the percent of salt indicated. In the first set of jars in Table 10, no salt was added, but the salt present in the pickles themselves brought the salt concentration to about 0.7%. The jars were examined two-and-a-half weeks after the tests were begun.

Table 10. - Bleaching effect of different salt concentrations on desalted pickles

	No salt added	2.5% Salt	3.8% Salt	5.0% Salt	15% Salt	20% Salt
Jar kept in light	-	-	-	-	-	-
Jar kept in dark	-	-	-	-	-	-

Discussion of Results

Salt alone was not responsible for the bleaching of pickles. Since salt stock bleaches with much greater difficulty than desalted pickles, salt in high concentrations does appear to inhibit bleaching.

Effect of metals and phosphates

To determine what effect metals or phosphates might have on dill pickles, 0.5 grams of various salts were added to jars of freshly desalted pickles. To some jars only water was added, and to others, dill brine. Examination of the jars was made in two weeks. The results are given in Table 11.

Table 11. - Effect of various compounds on color of desalted pickles

		Calcium Hydroxide	Calcium Chloride	Ferric Acetate	Magnesium acetate	Cuprous chloride	Zinc acetate	KH_2PO_4	Control
Water Only	Jar in Light	-		++	-	Pickles green because	+	+	-
	Jar in Dark	-		+	-		-	-	-
Dill Brine	Jar in Light	+	++	-	+	of Cu. Test useless	++	++	+
	Jar in Dark	-	-	-	-		-	+	-

Discussion of Results

Calcium chloride is used, in some cases, as a hardening agent, replacing alum. In the presence of light, it was responsible for whitening of the pickles tested. Whitening was produced experimentally, also, by the use of an iron salt, a zinc salt, and a phosphate. Whether these metals, or metallic salts, or phosphates produce, or contribute, to whitening under natural conditions, however, is another matter. In the ordinary pickle formula, none of these substances would be added intentionally to the pickles.

Effect of Vinegar

Every pickle formula contains vinegar, except for naturally fermented dill pickles. For processed dills, the composition varies from six to ten grains. Since eight grain vinegar seems to be about average, this was the concentration used in all the pickle tests.

Vinegar alone in water added to desalted pickles, and vinegar in combination with the ingredients used to prepare dill brine were subjected to tests to determine their effectiveness in removing pickle color. In addition, pickles were soaked in eight grain vinegar for one day and for four days prior to bottling in ordinary dill brine. The various combinations used, and the results of the experiments are charted in Tables 12 and 13. Observations were made on the pickles eight days after the tests were begun.

Table 12. - Bleaching effect of vinegar in combination with other ingredients on desalted pickles

	Jars kept in light		Jars kept in dark	
Vinegar Dilution Only	+	+	+	+
Vinegar + Salt	B	+	-	+
Vinegar + Alum	+	+	+	+
Vinegar + Spices	+		-	
Vinegar + Salt + Alum	+	+	+	-
Vinegar + Salt + Spices	+		+	
Vinegar + Alum + Spices	-		-	
Water Only	-	-	-	-
Full Dill Formula	+	-	B	-

Table 13. - Bleaching effect of soaking desalted pickles in vinegar before adding dill brine

	Soaked 1 day	Soaked 4 days
Bleaching results	±	+
	+	+
	+	+
	+	+

Discussion of Results

Twenty-four test jars of pickles containing eight grain vinegar showed some bleaching effect, in contrast to the controls without vinegar, which were all negative. Three jars exhibited a color loss in which about one-fourth of the two pickles was bleached, but the bleaching, in other cases, was small. A slight color loss occurred when the pickles were allowed to soak in vinegar for just one day (three of four positives) prior to bottling in dill brine, and a little more loss of color when the pickles soaked four days in vinegar. Of the eight experimental jars which did not show bleaching, five contained spices. If loss of color in these experiments was due to a lowering of pH, then perhaps the spice oils acted as a buffer to prevent any marked pH drop.

Effect of pH

The purpose of the experiments on pH was to determine whether whitening occurs only at certain pH's, or is independent of pH and will occur under any condition. The pH's were measured by means of the Beckman pH meter. Adjustment to the desired pH was made with the use of either glacial acetic acid or sodium hydroxide solution (either 18 molar or 4 molar, approximately). Salt stock pickles in their own brine and desalted pickles were used. Only the brine was adjusted; the pickles themselves were not taken into account. The brine was altered so the pH range was covered from pH 2 through pH 8. After adjustment, the pickles were exposed in their jars to direct sunlight for about two-and-a-half weeks (56 actual hours of sunlight).

Table 14. - Exposures of pickles of different pH to direct sunlight

	pH	No. of Hours Before Bleaching Occurred	Results of 56 Hours Exposure
Salt Stock + Salt Brine	2.0	6 1/2	++
	3.0	6 1/2 - 14	++
	3.5	0 - 6 1/2	+
	3.95	14 - 29	+
	4.58	6 1/2 - 14	++
	5.0	6 1/2 - 14	+
	5.56	29 - 53	+
	5.96	29 - 53	+
	6.46	0 - 6 1/2	++ -
	6.93	0 - 6 1/2	+
	7.58	0 - 6 1/2	++
	8.17	-	-
	3.95 Control Unexposed	-	-
Desalted Pickles + Dill Brine	2.02	0 - 14	+
	3.02	14	+
	3.22	29 - 53	+
	3.5	29 - 53	++
	4.01	0 - 14	++
	4.5	0 - 14	+
	5.0	29	B
	5.54	0 - 14	+
	6.0	29	+
	6.58	14 - 29	+
	7.08	14 - 29	+
	7.5	0 - 14	++
	8.02	29 - 53	+
	3.22 Control Unexposed	14 - 53	+

Discussion of Results

In this experiment, bleaching occurred at every pH from 2 to 7.58, inclusive, in the case of salt stock, and from 2.02 to 8.02, inclusive, in the case of desalted pickles. Whitening did not occur with equal rapidity at all pH's, however. In some cases, it was well marked at six-and-a-half hours (pH 2, salt stock), while in others, 29 to 53 hours were required for the color loss. The experimental work on this problem seems to indicate that loss of pickle color appears to be much more involved than the mere removal of magnesium from the chlorophyll molecule by an acid.

Effect of Alum

Alum, a standard ingredient in commercial pickle formulas, was used alone and in combination with other components of the dill pickle formula in the tests made. As was done with vinegar, desalted pickles were soaked in alum, for two days and for four day periods, at the termination of which they were bottled in dill brine. The amount of alum, $Al_2(SO_4)_3 \cdot 18\ H_2O$, was sufficient to give a final concentration of 0.1 percent by weight in the pickles and brine. In calculating the amount to use, allowance was made not only for the brine, but also for the water content of the pickles themselves. The results were recorded six days after the tests had been started.

Table 15. - Bleaching effect of alum in combination with other ingredients on desalted pickles

	Jars kept in light		Jars kept in dark	
Alum + Water Only	-	⊢	⊢	⊢
Alum + Salt	+	⊢	⊢	⊢
Alum + Vinegar	+	+	+	⊢
Alum + Spices	+	⊢	-	-
Alum + Salt + Vinegar	⊢		⊢	
Alum + Salt + Spices	⊢	⊢	⊢	-
Alum + Spices + Vinegar	B		-	
Water Only	-	-	-	-
Full Dill Formula	-	t	-	-

Table 16. - Bleaching effect of soaking desalted pickles in alum before adding dill brine

	Soaked 1 day	Soaked 4 days
Bleaching results	⊢	⊢
	+	+
	+	+ ⊢
	+ ⊢	++
	++	++ ⊢

Discussion of Results

Experimentally, the use of alum resulted in whitening of pickles in 28 out of 38 jars tested. Of the jars in which bleaching did not occur, nine of the ten jars contained spice oils combined with the alum. With alum, as with vinegar, it seems likely that the buffer action of the spice oils prevented the whitening of the pickles. The color loss in many cases was quite marked, especially where alum was combined with vinegar. When the pickles were first soaked in alum before being bottled, whitening occurred in every one of the ten jars, whose pickles had been previously soaked. The bleaching effect was considerable in these cases, as may be seen by reference to the last two columns of Table 16. The bleaching was only slightly greater when the pickles were soaked in the alum four days instead of two.

Effect of Turmeric

Most jars of pickles have oleoresin of turmeric added to improve the pickle color. The influence of turmeric seemed worth investigating in the belief that it might itself contribute to bleaching. Various combinations of turmeric and other components of the dill pickle formula were made up and added to jars of previously desalted pickles. The concentration used was 0.2 grams in ten gallons of dill brine. Observations on the jars were made in nine days.

Table 17. - Effect of oleoresin of turmeric on the bleaching of desalted pickles

	Jar in Light	Jar in Dark
Turmeric + Water	-	-
Turmeric + Alum	-	-
Turmeric + Spices	-	-
Turmeric + Salt	-	-
Turmeric + Vinegar	-	-
Turmeric + Salt + Vinegar	-	-
Turmeric + Salt + Spices	-	-
Turmeric + Salt + Alum	-	-
Turmeric + Alum + Spices	-	-
Turmeric + Alum + Vinegar	-	-
Turmeric + Spices + Vinegar	-	-
Turmeric + Salt + Alum + Spices	-	-
Turmeric + Salt + Alum + Vinegar	-	-
Turmeric + Alum + Spices + Vinegar	-	-
Turmeric + Salt + Spices + Vinegar	-	-
Turmeric + Full Dill Formula	-	-
Control--No Turmeric Full Dill Formula	-	-

Discussion of Results

Turmeric is used to improve the color of pickles, and this it did in this experiment. The color of the pickles was yellowed and deepened. In no case, in the 32 jars where turmeric was used, did any bleaching take place.

Effect of Storage

Pickles bleach in the pickle plant and on grocers' shelves. To determine whether storage is one of the factors responsible, salt stock in salt brine and desalted pickles in dill brine were stored for a month-and-a half. Observations on their color losses were recorded after one week (columns 2 and 3, Table 18) and after one-and-a-half months (columns 4 and 5). The difference in the amount bleached which resulted on storage from one week to the end of the month-and-a-half period are indicated in the last two columns.

Table 18. - Effect of storage for one-and-a-half months on bleaching of salt stock and desalted pickles

	Storage Period				Whitening on Storage between 1 Week & 1 1/2 Months	
	1 Week		1 1/2 Months			
	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark	Jar in Light	Jar in Dark
	-	-	-	-	-	-
Salt Stock Pickles + Salt Brine	-	-	-	-	-	-
	-		-		-	
	-		-		-	
	-		-		-	
	-		-		-	
	-	⊢	⊢	⊢	⊢	-
	±	±	+	⊢	+	⊢
	⊢	⊢	⊢	⊢	-	-
	+	-	+	-	-	-
Desalted Pickles in Dill Brine	⊢	-	++++	⊢	+++	⊢
	-	-	-		-	
	-		⊢		⊢	
	-		⊢		⊢	
	-		⊢		⊢	
	-		+		+	
	-		+		+	
	-		+++		+++	
	-		+++		+++	

Discussion of Results

The effects of storage were observed by examining twenty-six jars of pickles, eight of them salt stock pickles covered with salt brine, and sixteen, desalted pickles covered with dill brine. Of the salt stock pickles, none showed any color loss whatever, whether examined in a week or in a month-and-a-half after packing. In the case of the sixteen jars of desalted pickles, five jars showed bleaching in a week, and fifteen showed bleaching in a month-and-a-half. Of the five jars bleached in a week, one bleached further on additional storage. Only one jar of all sixteen failed to show any bleaching at all after a storage period of one-and-a-half months. In three jars, the pickles were almost completely whitened after a month-and-a-half; yet this effect was not at all apparent on early observation. Thus, whether pickle jars were examined in one week or in one-and-a-half months gave entirely different results in respect to whitening when desalted pickles were used, but the results were unchanged (all jars were negative) when salt stock pickles were observed.

Effect of Enzyme Inactivation

When the factors which resulted in bleaching were analyzed, they seemed to show a surprising correlation and a clear pattern pointing to enzyme activity in the pickles. For the reasons given below, the conviction that whitening was an enzyme activity seemed justified:

1. When bleaching occurred, it was always the blossom end which bleached first and more readily, never the stem end. Often the stem end was the only part of the pickle which did not lose its color. Since the blossom end is the active growing end, it would be expected that the enzymes would be more concentrated there, and there would be most active.

2. Vinegar seemed to cause bleaching in many cases. This effect appeared to be related to the optimum activity of the pickle enzymes, which, it could be expected, would function best at a lowered pH.

3. Alum, too, seemed to result in bleaching in many cases, and since this substance also lowers the pH of the pickles, it might be expected to provide more nearly optimum enzyme activity.

4. Infrared rays resulted in bleaching more consistently than any other factor. The reasoning along the pattern followed would naturally ascribe to the pickles the utilization of heat energy provided by the infrared radiation, and this energy should have accelerated enzyme activity. Sunlight, it seemed, play a similar role in stimulating enzyme activity by providing heat energy. It later became apparent that the action of sunlight was far more involved than the mere transfer of heat energy.

5. The function of storage in the bleaching process, it seemed, was to allow more time for enzymes to act. If whitening were an enzyme activity, then, obviously, enzymes would need a longer time to produce a bleaching effect if they acted slowly under conditions below their optimum.

6. Salt stock pickles whitened with much greater difficulty than did desalted pickles, and since it is known that salt in high concentrations inhibits enzyme activity, the case in favor of an enzyme explanation of whitening seemed convincing.

As a result of the strong conviction that enzyme activity held the key to pickle bleaching, a number of experiments were conducted to inactivate the pickle enzymes. It was felt that if the theory were valid, inactivation of the enzymes would prevent bleaching under all conditions, even if the pickles were exposed to direct sunlight, while the pickles with active enzymes (the controls) would still bleach.

In Table 19, ten jars of desalted pickles were treated to inactivate their enzymes, either by heat or by the addition of silver nitrate. This was a preliminary test to determine whether inactivation of the enzymes would bring about bleaching. Those jars which were kept in the light were exposed to the diffused light of the laboratory, and the others, as in other tests, were kept in the dark. Observations on the pickles were made in two weeks.

For Table 20, desalted pickles were heated from 70° C to 80° C for 10 minutes. Dill brine was first heated in a white porcelain pail until the brine was about 5° C. higher than the pickle temperature desired. Then pickles were added and the indicated temperatures maintained. Immediately after heating, the pickles were put in a jar with cold brine and the cap screwed on tightly. The jars of pickles were further cooled by running water. After the pickles had cooled, they were taken from the jars and exposed to infrared rays, or ultraviolet rays, or both, for fifteen minutes, five minutes one day and ten minutes the following day. The pickles were returned to the jars after treatment, and observations were made a month later.

The treatment given the pickles charted in Table 21 consisted in heating them in a vat in dill brine, followed by cooling, as for Table 20. The pickles were then taken out of the jars, dill brine was poured into a number of flat glass pans, and the pickles were placed in the pans, so that only the bottom surface of the pickles was covered by the brine. The rest of the pickles were above the brine, and in this manner the pickles were exposed to direct sunlight for ten hours.

For Table 22, pickles in pint Mason jars in dill brine were heated in an oil bath, using Wesson oil. A thermometer was inserted in one pickle of each set, and the temperature of the pickles held for the time indicated, 65° C to 95° C, from ten to thirty minutes. The pickles were cooled at the end of the heat treatment by removing from the jar, placing them in an empty jar, and running cold water over the jar. After the pickles were cooled, they were removed from the jars and exposed over dill brine in glass trays to direct sunlight for eight-and-a-half hours.

Desalted pickles (Table 23), were immersed in an excess of boiling dill brine in a wire basket, so that the boiling did not stop on addition of the pickles to the brine. The pickles were retained in the brine from one to fifteen minutes. They were rapidly cooled on removal by being dipped in cold, refrigerated dill brine. Following this heat treatment, the pickles were placed in glass trays over a shallow layer of dill brine, and exposed to direct sunlight for seven hours.

Table 19. - Results of treating desalted pickles to inactivate their enzymes

		Pickles & Brine boiled 10 min.	Pickles & Brine heated to 80° C. for 10 min.	Pickles put in boiling brine for 10 min.	0.5 gm. silver nitrate added	Controls unheated
Dill Brine	Jar in Light	-	±	-	-	+
	Jar in Dark	-	-	-	-	-
Water Only	Jar in Light				++	
	Jar in Dark				-	

Table 20. - Results of heating desalted pickles, followed by exposures to infrared and ultraviolet rays

	Heat Treatment						
	71° C-- 10 min.	70° C-- 20 min.	75° C-- 15 min.	77° C- 10 min.	80° C-- 5 min.	80° C- 10 min.	Con- trols
Exposed to Infrared Rays 15 min.	+	++	+	+++	++	+	+
Exposed to Ultraviolet Rays 15 min.	+	+	++	+	+	+	+
Exposed to I. R. 15 min., then U. V. 15 min.	+	++	+	+++	++	+	+
Control-- No Exposure	+	+	+	++	++	B	+ +

Table 21. - Results of heating desalted pickles, followed by exposure to direct sunlight

	Heat Treatment										
	70°C 30 min.	75°C 30 min.	77°C 20 min.	77°C 30 min.	80°C 15 min.	80°C 30 min.	85°C 10 min.	85°C 20 min.	85°C 30 min.	90°C 10 min.	Control Not Heated
Exposed to Sun	++	+++	++	+	++	++	+	+	++	+	++
	++	+++	++	+	++	++	+	++	++	++	++
	+++	+++	+++	++	++	+++	++	++	+++	++	+++
	+++	+++	+++	+++	+++	+++	+++	++	++++	++	+++
Not Exposed	-	-	-	-	+	+	-	-	-	-	-
	+	-	+	+	+	+	++	+	+	-	-

Table 22. - Results of heating desalted pickles, followed by exposure to direct sunlight

	Actual Pickle Temperatures									
	65°C for 10 min.	65°C for 20 min.	65°C for 30 min.	75°C for 10 min.	75°C for 30 min.	80°C for 10 min.	85°C for 30 min.	95°C for 10 min.	Controls-- Not Heated	
Exposed to Sun	+	+	++	+	+	+++	++	++	++	
	++	++	++	++	++	+++	++	++	++	
	++	+++	+++	++	+++	+++	++	++	++	
	+++	+++	+++	++	+++	++++	+++	+++	+++	
Not Exposed to Sun	-	-	-	-	-	-	-	-	-	-
	-	-	-	-	-	+	+	-	-	-

Table 23. - Results of immersing desalted pickles in boiling dill brine, followed by exposure to direct sunlight

	Time of Heat Treatment							
	1 Min.	2 Min.	3 Min.	5 Min.	7 Min.	10 Min.	15 Min.	Controls-Not Heated
	++	+++	++	+++	++	++	++	++
Exposed	++	+++	+++	+++	+++	+++	++	++
to Sun	+++	+++	+++	+++	+++	+++	+++	+++
	++++	+++	+++	++++	++++	++++	+++	+++
Not	-	-	-	-	-	-	-	- -
Exposed to Sun	-	-	-	+	-	-	-	- +

Discussion of Results

From Table 19, it may be seen that in the experiments to determine whether the process of inactivating enzymes would itself produce bleaching, the results appear to be negative. Of the ten jars tested, only one was definitely bleached, and that, by the use of silver nitrate. It may be, in the case of the jar which showed bleaching, that the sodium chloride in the pickles and the pickle brine reacted with silver nitrate to form silver chloride, and this silver chloride coating was the whitened pickle. The other nine jars were negative, and showed no bleaching.

By means of various treatments, 188 pickles, exclusive of controls, were subjected to heat sufficient, it was believed, to inactivate their enzymes. The temperatures of heat treatment ranged from 65° C. to at least 95° C.

As indicated in Table 20, pickles which had been subjected to temperatures such that dill brine plus added pickles reached 70° C. to 80° C. for ten minutes, showed definite bleaching after exposures to infrared and ultraviolet rays in every single jar; in most cases the bleaching was more extensive in the exposed pickles which had previously been heated than in the exposed pickles which had not had any previous heat treatment. Thus, in this experiment, heat treatment neither prevented the whitening of pickles, nor retarded such action in any way.

For Tables 21, 22, and 23, pickles were directly exposed to the sun outdoors on successive clear days for the total time indicated.

The drastic treatment, it was felt, would show the effect of enzyme inactivation without question, whether enzyme inactivation inhibited whitening, or prevented it. If pickles which had been heated, at least those which had been heated to high temperatures, and which were of good color before exposure to the sun, did not lose their color on exposure, it might be concluded that enzymes were no longer able to effect a color loss (since they had been inactivated or denatured), and thus the evidence would indicate that whitening was an enzyme activity. In other words, color loss would result, under such conditions, only if active enzymes were present; if enzymes were inactivated, no color loss would occur. Of the 100 heat-treated pickles exposed to the sun, however, every single one, without exception, turned white, as may be seen by examination of Tables 21, 22, and 23. The color loss, in almost every case, was very marked; in 22 cases, at least half of the pickle was bleached; in some cases, the entire pickle was bleached. In 90 of the 100 pickles, more than a third of the pickle suffered a loss of color. There seemed to be no noticeable difference in the bleaching effect whether the pickles were heated or not prior to exposure to sunlight. In other words, heat treatment, including, as it does, enzyme inactivation, did not seem to make any difference in the ability of the pickle to turn white. Nor did the manner of heating the pickle affect the results in any way, whether the pickles were immersed in a vat and heated, whether the pickles were heated in a jar with a thermometer stuck inside a pickle until the temperature reached the desired height, or whether the pickles were immersed in boiling brine, somewhat in the manner of blanching. These experiments seemed to erase the belief that pickle bleaching is purely an enzyme activity. In not one case did there seem to be any relation between heat treatment, or enzyme inactivation, and the inhibition of bleaching.

Effect of Oxidation

In attempting to unearth the factors or causes for pickle bleaching, the hypothesis that bleaching is an oxidative process was subjected to several tests. The results are tabulated in Tables 24-30, inclusive.

The experiments which Table 24 records were undertaken in order to determine whether oxidizing or reducing agents affect bleaching. The chemical substances were added in the amounts indicated (or heat was applied) and the jars were observed three weeks later.

For the work recorded in Tables 25 and 26, oxygen was introduced into a number of pickle jars by two different laboratory methods of generating the gas. It was felt that if oxidation were responsible for bleaching, then pure oxygen should greatly accelerate the bleaching process.

For Table 25, oxygen was obtained by the use of an oxygen generator, which consisted of a separatory funnel with water leading into a flask containing sodium peroxide. The gas was washed by passing from the generator through a flask containing distilled water before being led to the pickle jars. After the jars had been given their measured supply of oxygen gas, they were either exposed to direct sunlight, or kept in the dark.

The oxygen for Table 26 was generated by heating mercuric oxide. It was washed by being led through a flask of distilled water. The heat applied was adjusted so that there was very nearly a constant flow of 82 bubbles of gas per minute. Desalted pickles only were used. The jars were left in the diffused light of the laboratory for three weeks and then observed for change.

For Table 27, the pickles were boiled--salt stock in salt brine and dill pickles in dill brine--in the jars in an oil bath. The jars were capped tightly while boiling was taking place. To indicate the effectiveness of this method of air removal, each jar was tested for amount of vacuum at the time the results were recorded. (Three jars of salt stock pickles had a vacuum of 24.5 in. and one jar, of 23 in. Two of the jars of desalted pickles had vacuums of 25 in.; one was 24 in.; and one was 23.5 in.). After the jars had cooled, they were exposed outdoors for about half a month on clear days, and then all day long for another half month.

In Table 28, 0.5 gram portions of antioxidants were added to jars of desalted pickles in dill brine to give a concentration of about 0.1 percent antioxidant. This work was undertaken to determine whether antioxidants might be a contributing factor in pickle bleaching. The work outlined in Tables 29 and 30 could not have proceeded without a prior knowledge of the influence on pickles of the antioxidants themselves.

Tables 29 and 30 show the results obtained after exhausting the air from jars of desalted pickles in dill brine. The jars of pickles were placed in a dessicator and evacuated by means of a Cenco vacuum pump. A vacuum of about 73.5 cm. was obtained in this way. To prevent leakage, the inert gas, nitrogen, was then introduced into the dessicator from a tank of pure nitrogen until pressure, equal to atmospheric pressure, was restored, as indicated by the manometer. The evacuation and substitution was done three times. Five-tenths of a gram of various antioxidants were then added to the jars to give a concentration of about 0.1 percent antioxidant, and the cap was screwed on tightly. The jars were then exposed to direct sunlight in the same way as for Table 27.

Table 24. - Bleaching effect of oxidizing and reducing agents on desalted pickles

		REDUCING AGENTS				OXIDIZING AGENTS		
		Boiled 10 min. to remove oxygen	1 gm. Cu_2Cl_2 in HCl added to absorb O_2	10 small nails added to jar	3 ml. H_2SO_3 added	.5 gm. $KMnO_4$ added	1 gm. KIO_3 added	.5 gm. Calcium Hypochlorite added
Dill Brine	Jar in light	-	Test Useless.	⊢	-	-	+++	+
	Jar in dark	-	Greening	-	-	-	⊢	-
Water	Jar in light		Resulted	-	+	±	-	-
	Jar in dark			-	+	pickles turned brown	-	+

Table 25. - Bleaching effect of oxygen gas added to jars of pickles, followed by exposing jars to direct sunlight, or storing them in dark

		Oxygen Introduced into Jars 5 min.	Controls--No Oxygen
Salt Stock in Salt Stock Brine	Jars Exposed to Sun for 4 Hours	-	⊢
		-	
		-	
	Jars Kept in Dark	-	B
		-	
		-	
Desalted Pickles in Dill Brine	Jars Exposed to Sun for 4 Hours	+	⊢
		+	
		+	
	Jars Kept in Dark	+	⊢
		+	
		⊢	

Table 26. - Bleaching effect of oxygen gas introduced into jars of pickles, followed by exposing them to diffused light

	Results
Oxygen Introduced into Jars for 5 min.	++
	+
	+
	+
	+
	⊢
	⊢
	⊢
	⊢
Controls--No Oxygen	+
	+
	+
	+
	⊢
	⊢

Table 27. - Bleaching effect of boiling pickles in jars for 10 minutes, followed by exposing jars to direct sunlight

	Salt Stock Pickles in Salt Brine		Desalted Pickles in Dill Brine	
	Pickles & Brine Boiled	Not Boiled	Pickles & Brine Boiled	Not Boiled
Exposed to Sun				⊢
	B	⊢	⊢	⊢
	+	⊢	+	+
Not Exposed	-	-	-	-
	B		B	

Table 28. - Bleaching effect of 0.1% antioxidant on desalted pickles

		Hydro-quinone	Alpha Naphthol	Leci-thin	Cate-chol	Control
Water Only	Jar in Light	-	±	+	-	-
	Jar in Dark	-	-	-	-	-
Dill Brine	Jar in Light	-	-	⊢	-	±
	Jar in Dark	-	-	-	-	±

Table 29. - Bleaching effect on salt stock pickles of removing air, substituting nitrogen, adding 0.5 gram antioxidant, and exposing pickles to direct sunlight

	Ascorbic & citric acid added		Pyrogallol added		Pyrogallol & NaOH added		Catechol added		Hydroquinone added		Alpha naphthol added		No antioxidant added	
	N_2 for air	Air not removed	N_2 for air	Air not removed	N_2 for air	Air not removed	N_2 for air	Air not removed	N_2 for air	Air not removed	N_2 for air	Air not removed	N_2 for air	Air not removed
Exposed to Sun	+	+	±	B	+	+	B	+	B	+	B	+	+	B
	+						+		+		+		+	+
													+	+
														+
														+
														+
Not Exposed	-	B	-	B	-	-	-	B	B	-	-	B	-	-
													-	B
														-
														+

Table 30. - Bleaching effect on desalted pickles of removing air, substituting nitrogen, adding 0.5 gram antioxidant, and exposing pickles to direct sunlight

	Ascorbic & citric acid added		Pyro-gallol added		Pyro-gallol & NaOH added		Catechol added		Hydro-quinone added		Alpha Naphthol added		No anti-oxidant added	
	N_2 put in for air	Air not re-moved	N_2 put in for air	Air not re-moved	N_2 put in for air	Air not re-moved	N_2 put in for air	Air not re-moved	N_2 put in for air	Air not re-moved	N_2 put in for air	Air not re-moved	N_2 put in for air	Air not re-moved
	+	+	⊢	⊢	⊢	+	⊢	⊢	⊢	+	B	B	-	+
Ex-	+						⊢		+		⊢		⊢	+
posed													⊢	++
to														++
Sun														+⊢
Not	B	-	-	-	-	-	-	-	-	⊢	⊢	-	B	⊢
Ex-													B	-
posed														+

Discussion of Results

By reference to Table 24, it may be seen that neither oxidizing nor reducing agents, as a group, caused whitening. Where whitening occurred, the reasons, very likely, may be found in the characteristics of the individual substances used. Thus, sulfurous acid, potassium iodate, and calcium hypochlorite are known to have bleaching properties. Oddly enough, however, these substances did not cause bleaching of pickles in all circumstances, but all of them did cause bleaching in some jars.

In Table 25, it may be seen that when salt stock pickles were used, the jars into which oxygen had been introduced for five minutes showed no bleaching at all, whereas only the controls without added oxygen were whitened. In the case of desalted pickles (Tables 25 and 26), every jar containing introduced oxygen showed whitening; but so did the controls, to which no oxygen had been added. Moreover, the bleaching effect in the eight control jars was about as marked as the bleaching in the fifteen other experimental jars.

As may be seen by reference to Table 27, the seven jars of pickles which had been boiled showed substantially the same results as the eight jars of pickles which had not been boiled. Bleaching resulted to some extent in all the jars, but the bleaching was not marked. Of the jars subjected to boiling but not exposed to the sun, there was little, if any, loss of color at all, and the results were exactly the same in the case of the jars not subjected to boiling.

It is known that antioxidants are preferentially oxidized and that this characteristic prevents oxidation of the substrate. If the controls in Table 28 had been bleached and the experimental jars had not, it could have been interpreted as an indication that oxidation caused the bleaching. Under such conditions, the removal of free oxygen from the pickle jars by the oxidation of the antioxidant would leave none free to cause whitening of the pickles, whereas the presence of oxygen in the controls would bleach them. The controls did not whiten, however; neither did the pickle jars containing antioxidant, except for two jars in which lecithin had been used. Thus, it seems reasonable to assume that bleaching is not a simple oxidation process, at least not a union of the pickle with oxygen merely.

In Table 29, of six jars evacuated and given nitrogen gas to replace the air, five showed a slight amount of bleaching after completion of their periods of exposure to the sun. By comparison, of the 11 controls which had not been evacuated, but were exposed at the same time, five jars showed an equal amount of bleaching and six jars showed an amount greater than that exhibited by the experimental jars. The pickles in the jars from which air had been removed, which were not exposed, did not bleach, whereas, by comparison, three of the seven jars neither evacuated nor exposed did show a small degree of color loss. There was, then, a little more bleaching in the case of the jars which had retained their air.

Of the jars both evacuated and treated with antioxidant, and exposed to direct sunlight as well, seven showed almost no whitening, 19 showed only a very small amount, and six showed whitening of about 1/6 of each pickle in each jar, actually not a great amount of bleaching. Of the 24 jars of pickles containing antioxidant, whether previously evacuated or not, there were only two jars whose color losses were noticeable, and in them the bleaching effect was very small.

To summarize, of the 42 jars of pickles exposed to sunlight which had been treated in some way to inhibit, or eliminate, oxidation--by exhausting, evacuating with a vacuum pump, treating with an antioxidant, or both evacuating and treating with antioxidant--very little bleaching occurred, though nearly every jar did show slight color loss. In only eight jars was there as much as 1/6 of the pickle bleached. Of the 16 control jars of pickles, untreated in any way, but exposed to direct sunlight, three jars showed more bleaching than any of the experimental jars, five showed as much as the largest amount of bleaching shown by the eight experimental jars, and eight showed color losses comparable in amount to those which 35 of the 42 experimental jars showed. Of the jars not exposed to the sun, 29 of the 31 jars treated to eliminate oxidation by the methods mentioned showed no appreciable color loss, as compared with seven of the ten controls which were negative, or nearly so. Two of the experimental jars showed a slight amount of bleaching, as compared with one control jar. In addition, two other control jars were bleached to a greater extent than any of the 31 experimental jars.

Elimination of oxygen, then, inhibited bleaching only to a slight extent, if at all.

If bleaching were an oxidative process involving oxygen, it might be expected that the addition of oxygen to the jars of pickles would enhance whitening. Tables 25 and 26 make it clear that the addition of oxygen did not have any material effect on the pickles so treated. Together with the experimental work on evacuation and antioxidants, this fact forms more complete and convincing evidence that oxidation with oxygen is not the simple factor which brings about the loss of pickle color. It may be true, however, that pickles in brine have a maximum, or optimum, amount of oxygen already, and that any more would not have an additive effect. In other words, the fact that addition of oxygen to the pickles did not seem to make any difference in their activity probably neither proves nor disproves the theory that oxidation with oxygen is a factor, or cause, of pickle bleaching.

Combined Effect of Enzyme Inactivation and Oxygen Removal

Working on the assumption that perhaps a single factor alone--enzyme activity or oxidative reactions--might be an oversimplification and an unworkable approach to the complex problem of pickle bleaching, the work of Table 31 was next undertaken. It was reasoned that even if both factors were responsible for pickle bleaching, the absence of one might be masked by the continued activity of the other. So it was decided to eliminate both. Enzymes were inactivated, it was believed, by heating the pickles in a vat in dill brine to temperatures ranging from 70° C. to 85° C. for the times indicated. The pickles, after removal from the vat, were placed in jars, cold brine was added, and the pickles were further cooled by directing running water over the jars. Then the oxygen, or air, was removed, and nitrogen was substituted. Finally the jars were exposed to direct sunlight for about a month.

Table 31. - Bleaching effect on desalted pickles of heating, removing air, substituting nitrogen, and exposing to direct sunlight

	Heat Treatment											
	70° C.-- 23 min.		70° C.-- 30 min.		75° C.-- 15 min.		75° C.-- 30 min.		85° C.-- 15 min.		Controls- No Heat - Treatment	
	Evac-uated	Not Evac-uated	Evac-uated	Not Evac-uated	Evac-uated	Not Evac-uated	Evac-uated	Not Evac-uated	Evac-uated	Not Evac-uated	Evac-uated	Not Evac-uated
Ex-	+	+	⊢	⊢	B	B	⊢	⊢	⊢	⊢	B	⊢
posed	-		+		B		⊢		B		⊢	+
to Sun											⊢	+
Not	-	-	-	-	-	-	-	-	-	-	-	⊢
Ex-											⊢	B
posed												B

Discussion of Results

In ten jars which had been both heated to inactivate enzymes and evacuated to prevent oxidation, loss of color was very slight on exposure of the jars to direct sunlight for about a month. In only two of the jars was as much as 1/6 of the pickles affected by bleaching. Yet, compared with this result, five jars which had not been evacuated, but heated only, showed essentially the same results on exposure to the sun's rays. So, too, did the controls, to which no heat had been applied. In other words, the end result, as far as bleaching of pickles was concerned, was about the same whether

1. The pickles had been heated only before exposure,
2. The pickles had been evacuated only before exposure,
3. The pickles had been heated and evacuated before exposure,
4. The pickles were exposed without any treatment at all.

Those jars which had not been exposed to the sun showed no color loss in the cases where heat had first been applied, but showed some evidence of bleaching in four of five jars which had had no prior heat treatment. Perhaps the combination of these two factors, enzyme inactivation and reduction of oxygen, does inhibit whitening under normal conditions, but not under conditions as drastic as direct exposure to sunlight.

SUMMARY

Salt stock and desalted pickles were exposed to various conditions in an attempt to determine the factors which produce bleaching of pickles, and if possible, to find the underlying causes for bleaching.

Salt stock pickles of 60° salometer did not bleach as readily as did desalted pickles in these experiments. Pickles in jars, either salt stock in salt brine, or dill pickles in dill brine, bleached to a lesser extent, with much greater difficulty, and after longer time exposures than did similar pickles out of jars.

The most potent factor in bleaching was direct sunlight. When desalted pickles were exposed out of jars, almost complete bleaching occurred in as little as 4 1/2 hours, in some cases. By contrast, similar pickles showed comparatively little color loss when they were placed in jars.

It was the infrared rays in the sun's spectrum which consistently produced the clearest cases of whitening. Bleaching resulted whether salt stock was used or whether desalted pickles were used, and whether the pickles, after exposure, were kept in the light or in the dark. It occurred whether the pickles alone were exposed to infrared rays, or whether the pickles and the brine were exposed together. It did not occur, however, when the pickles were completely covered by salt stock brine, though when the pickles were not completely submerged, bleaching did usually result. Bleaching occurred just as readily in the pickles when the packed jars, covered with brine, were exposed to infrared rays as when pickles were exposed to the rays outside the jar.

Ultraviolet irradiation produced marked bleaching in some cases. The evidence, however, is rather confusing, since loss of color, to an extent greater than that in the controls, occurred in little more than half the samples. Many pickles, on exposure to ultraviolet, failed to show any bleaching effects, even though the periods of exposure were long ones. This was true both for salt stock and desalted pickles. The germicidal band was the part of the ultraviolet spectrum which was principally, but not exclusively, used.

Eight grain vinegar caused bleaching to a slight degree. This bleaching effect resulted when pickles were soaked in vinegar from one to four days before bottling. It also occurred when vinegar was used alone, or in combination with various ingredients, but it did not occur when vinegar was used with both alum and spices.

In the jars tested, bleaching seemed to occur with nearly equal facility at every pH, from 2 through 8, whether salt stock or desalted pickles were used.

Alum alone, or alum combined with vinegar or salt, produced bleaching consistently. Loss of color was quite marked when desalted pickles were soaked in alum from two to four days prior to bottling. When alum was used as one of the components of dill brine, however, bleaching did not occur.

The effect of storage on dill pickles in jars was to enchance the bleaching process considerably, when the jars were exposed to the diffused light of the laboratory. Almost all the jars examined exhibited a marked increase in bleaching when color losses over a period of a month-and-a-half were compared with those undergone over a period of a week. By contrast, salt stock pickles showed no color loss whatsoever over the long exposure period.

Several salts were used on desalted pickles. Of these, calcium chloride, zinc acetate, and potassium dihydrogen phosphate caused marked bleaching of pickles.

Differences in temperature had little effect on the color of pickles, when temperatures ranging from 12° C. to 37° C. were used.

Differences in salt concentration did not lead to any clues in the search for factors that cause whitening, since the pickles with salt concentrations from 0.7 to 20 percent were all negative to color changes.

Tests made with spice oils in the concentrations used in processed dill pickles showed some conflicting results. In the main, however, the combination of spice oils as an emulsion, used in the manner employed in the pickle plant, yielded negative results.

The use of oleoresin of turmeric yellowed and deepened the pickle color and favored color retention in the pickles, but its use did not, in any case, result in loss of pickle color.

The treatment of pickles by heat and silver nitrate to inactivate the enzymes, showed that enzyme inactivation does not itself contribute to whitening. No bleaching resulted, except in one case where silver nitrate was used. The bleaching appeared to be a precipitation of silver chloride rather than a bleaching caused by enzyme inactivation.

Several experiments were undertaken in an attempt to determine whether inactivation of enzymes would inhibit, or completely prevent, pickle bleaching. Different methods of heat treatment were used, including heating of pickles in and out of jars from temperatures of 65° C. to 100° C., and from periods of one to thirty minutes. The pickles so treated were then exposed to direct sunlight. From the results tabulated, it is evident that heat treatment, or enzyme inactivation, did not show any inhibition of bleaching whatsoever.

The belief that oxidation might be an important factor in pickle bleaching was put to test in a number of ways. Various oxidizing and reducing agents were first tested for color loss which they themselves might inflict. Those which showed a positive effect were all bleaching agents. When antioxidants were used, they did not cause pickles to lose color, except when lecithin was employed and the jars were kept in the light. The addition of oxygen gas into jars had no apparent effect on bleaching either, contrary to what had been expected.

In another group of experiments, air was removed from a number of jars and the inert gas, nitrogen, substituted. In some cases, in addition to evacuation, antioxidants were added to eliminate any residual oxygen present. Still another method used was to exhaust the air by boiling, after which the jars were quickly closed. On exposure of these jars to direct sunlight, no clear inhibition of bleaching resulted.

The combined heat treatment, evacuation of air, and substitution of nitrogen did not show any certain evidence that retardation of bleaching in pickles had been effected.

CONCLUSIONS

In the experiments undertaken, these were the factors which resulted in bleaching pickles:

1. Direct sunlight
2. Infrared rays
3. Storage
4. Alum, to a slight extent
5. Vinegar, to a slight extent
6. Under certain conditions, ultraviolet rays.

It is obvious from this report that only a beginning has been made in exploring the problem of pickle bleaching.

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