DIFFUSION RATE OF DYE IN PREPARATION OF MARASCHINO CHERRIES

by

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CHAPTER I

INTRODUCTION

Fruit cocktail and fruit salad, which were first commercially canned in the period of 1925 to 1930, are now very popular. Since their beginning, the production has increased and in 1949 had a total production of 8,158,324 actual cases of all can sizes.

Although there is a slight difference between canned fruit cocktail and fruit salad, each contains Maraschino cherries. With the general increase in the production of the fruit cocktail and fruit salad there is a corresponding increase in the consumption of Maraschino cherries, the reason being that with each number 2 1/2 can (one pound fourteen ounces) the Maraschino contents are not less than three percent nor more than six percent of the total drained weight. Table I, acquired from the 1950 edition of the "Western Canner and Packer Statistical Review and Yearbook" (18) confirms the increased production of Maraschino cherries which were used exclusively in the canning of fruit cocktail and fruit salad.

TABLE I

Indicated U.S. Manufactured Cherry Packs

(Thousand of Gallons)

Period	Cherries used in Cocktail and Salad
1926-30*	140
1931-35*	300
1936-40*	420
1941-45*	590
1946	830
1947	990
1948	1,090
1949**	720

*Average of years shown

**Represents only part of total, balance carried over in 1950 season.

The mandatory Food and Drug food standard for quality in canned fruit cocktail, effective November 16, 1942, states that when artificially colored cherries are used, the appearance of canned fruit cocktail is controlled, along with other factors, by the uniformity of color of the units of cherry ingredient. Artificial coloring does not contribute the same intensity of color to all cherries and for this reason a tolerance has been set.

The artificial dyes permitted by pure food laws and used in the preparation of Maraschino type cherries

are Ponceau 3R, Amaranth and Erythrosine. Of the three red dyes only Erythrosine is suitable for dyeing Maraschino cherries used in fruit cocktail or fruit salad. Ponceau 3R and Amaranth are water soluble acid dyes and will easily discolor the sirup and stain the surrounding fruit, thus giving an unattractive product. Erythrosine, a water soluble acid dye, is easily "fixed" in the cherry tissue by treatment with a weak acid. With the dye "fixed" in the cherry tissue, an attractive pack can be prepared for the consumer.

The greatest problem is obtaining a rapid and uniform penetration of the Erythrosine dye into the cherry and not allowing the dye to discolor the fruit. Work has been done by Strachan (14) and Van Blaricom (16) on the factors influencing the dyeing of the cherries and affecting the stability of the Erythrosine dye. In view of their work and that of others, it was felt that a more uniform product could be prepared with the use of a non-toxic wetting agent. It was thought that by subjecting the Erythrosine dye solution to proper conditions, a rapid and uniform color penetration could be obtained in less heating time. This would result in an product of appetizing

appearance, which is a relatively important factor in its quality.

The objectives of the experiment were:

1. Determination of the rate of diffusion of the aqueous solution of Erythrosine dye with and without the wetting agent.

2. Determination of the suitable procedures in application of dye-wetting agent combination.

3. Retention of the dye when in contact with fruit and sirup during the processing and storage.

The manufacturers, by following the accepted procedure for dyeing cherries, usually obtained satisfactory results. The procedure used in dyeing cherries is to place the brined cherries in running water for a period of twenty-four hours and then boil them in fresh water for a designated period of time. The cherries are then dyed, with the aid of heat, in a 0.1 percent Erythrosine dye solution until, by penetration, the desired shade is reached. Two different pH's of the dye solution are used, one at about 4.4, Bullis and Wiegand (3), and the other 7.5 as suggested by Jeffery and Cruess (8). The dye is fixed with citric acid solution at pH of about 3.0 to 3.8.

The following list of words are those terms which will be used throughout the written material. The definitions are given to help the reader in his understanding of the manuscript.

Acid set	Treatment of the dyed cherries with an acid solution which penetrates some distance from the surface, providing an acidified zone which will serve to prevent dye movement and will also absorb any dye which diffuses from the central tissue which would normally discolor the adjoining fruit.
Bleeding	Red discoloration caused by residual dye on the other fruit in the cocktail or salad pack.
Leaching	Removal of the sulfur dioxide contained in the brine used to preserve the cherries. This is done by continous washing for approximately twenty-four hours and then boiling the cherries several times in fresh water

Optical density	The logarthm of the reciprocal of the intensity of transmitted light. The measurement is affected by a change in a concentration of absorbing material.
Surface tension	The surface tension of a liquid is the force in ergs per square centimeter on the surface of a liquid which opposes the expansion of the surface area.
Wetting agents	Compounds which cause variation in the surface forces of a liquid in relation to other liquids, gases or solids. Other names are surface active agents, spreading agents, penetrating agents, foaming or anti-foaming agents, detergents or floatation agents.

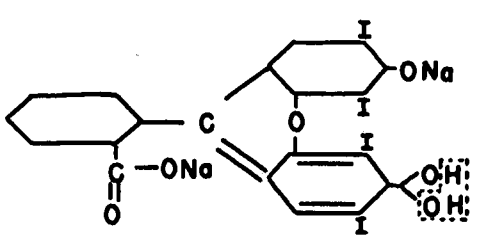
CHAPTER II

REVIEW OF LITERATURE

Erythrosine and Factors affecting its stability:

The use of colors in foods is a practice which has existed from ancient times. The colors that may be placed into foods are classified into three groups: (1) Coal tar dyes or artificial coloring matter, (2) natural or vegetable colors and (3) mineral colors or inorganic dyes. With the advent of synthetic coal tar colors, the use of color in foods began immediately to increase. The use of coal tar colors in foods in the United States was first legalized by an act of Congress, August 2, 1886, but not until 1907, with Food Inspection Decision number 76, did the colors become certified by the Department of Agriculture.

Erythrosine, a coal tar dye, was discovered in 1875 although the sodium salt purification was not known well even in 1909. Gomberg and Tabern (5) in 1923 established the structual formula of Erythrosine to be:



This structure of Erythrosine, a sodium salt of tetra-iodofluorescein, was later confirmed by Wales and Nelson (17) in 1923, and by Holmes and Scanlan (6) in 1927. They agreed that the structure contains the equivalent of one molecule of water held tenaciously in the molecule and that it is impossible to remove this molecule of water without destroying the coloring matter itself.

Ambler (2) stated in 1926 that Erythrosine is a brown powder which dissolves in water to form a cherry red solution, and is prepared by iodenating fluorescein, a dye made by condensing phthalic anhydride with resorcinol. Erythrosine is insoluble in all the usual solvents which boil below 100°C with the exception of alcohol and then only slightly in it. When HCl is added to its solution a yellow brown precipitate of the free color acid is produced. This color acid is insoluble in water and is precipitated from solutions of the dye even by very weak acids. For this reason Erythrosine is not suitable for use in beverages which have acid reactions, but is suitable for preparation of Maraschino cherries because the acid "sets" or precipitates the dye in the cherry tissue.

In 1929 Jeffrey and Cruess (8) described the H ion concentration as the dominating factor influencing

the rapidity, uniformity, diffusion and fixation of the dye. At pH lower than 4.0 the solubility of Erythrosine decreases markedly and when the pH of the dyed cherry is at 6.7 the bleeding is rapid, appreciable at pH 4.7 and very slight at 3.8. A difficulty is encountered in taking pH readings of the dye, since it is a sodium salt of a weak acid which will affect the pH values at low acidities, for sometimes it requires two months for the dye to reach equilibrium.

Strachan (14) in 1939 suggests that the calcium content, degree of leaching, the sulfur dioxide content and presence of metal ions have varying effect on the diffusion of the Erythrosine dye; but he also states that the hydrogen ion concentration is the dominating factor.

Properties of Wetting Agents:

The use of wetting agents in fruits and vegetables was reported by Olsen (11) in 1941. In most cases the addition of the wetting agent is used in the washing and peeling process giving speedier and more uniform results. Schwartz and Perry (13) in 1949 say the effect of adding the wetting agent in an aqueous solution has a lower surface energy and therefore the penetrating power of the solution is increased.

The literature referring to wetting agents is lengthy and covers an enormous amount of material. The products of three manufactures were selected and used in the experiment. They are Aresket, a Monsanto Chemical Company product; "Naconnol N R" manufactured by National Aniline and Chemical Company and D-40 manufactured by the Oronite Chemical Company.

The Monsanto Technical Bulletin No. P-113 (10), Oronite Chemical Company Technical Bulletin D-40 (12), and Naconnol N R (1) state the relative values of the three wetting agents. The characteristics of these wetting agents required for this experime stated in the three Technical Bulletins are non- toxicity, powerful surface tension depressant at tremely low concentrations, high degree of rinsi so that it may be easily removed with a minimum rinsing, chemical stability in a wide variety of it might encounter such as acid and alkaline solutions, non-decompotition of the wetting agent on standing in aqueous solution, readily and completely soluble in soft or hard water, neutral in reaction, cheapness to the industry, not oxidized to give off flavor, and stable in contact with metals and metallic salts.

The three wetting agents chosen are alkyl aryl sulphonates, products of petroleum sulphonation, and had previously been used in connection with fruits and vegetables.

CHAPTER III

EXPERIMENTAL STUDY AND PROCEDURES

The general plan of experimental procedures was to first ascertain the proper concentration of non-toxic wetting agent and solution of the Erythrosine dye to be used in dyeing the cherries and at the same time to determine the pH at which the combination was stable. The problem then was to determine whether the dye did diffuse quicker into the cherry tissue than when the conventional procedure for dyeing Maraschino cherries was used. The remaining study was determining the amount of residual wetting agent in the prepared cherries and in testing their bleeding against a control prepared by the conventional methods.

Concentration of Erythrosine:

The concentrations of Erythrosine recommended by different authors are numerous and vary considerable. The extremes cited concerning the concentration are Cruess (4), who states that a 0.02 to 0.05 percent solution is used, and Turner (15), who recommends one and one half ounces per twelve gallons of water, 0.094 percent. Bullis and Wiegand (3) recommend three quarters

to an ounce of dye per one hundred pounds of cherries, 0.05 to 0.06 percent. For this experiment the concentrations decided upon were 0.04, 0.06 and 0.1 percent aqueous solutions of the dye. It was felt that this covered the range recommended and gave to the solution enough dye to give the cherry the desired red shade.

Concentration of non-toxic wetting agent:

It would have been extremely difficult to predict the amount of wetting agent required to depress the surface tension. However, from graphs and technical data it was found that the surface tension of a solution decreases rapidly with a small increase in concentration of wetting agent. It tends to straighten out at 0.1 to 0.15 percent and then with further addition proceeds parallel to the coordinate axis. The amount of wetting agent needed to reduce the surface tension so that a higher penetration of the dye would be possible and still not have an excess amount, was thought to be in the range of 0.025 to 0.075 percent. These were the two extremes and another concentration of 0.05 percent was added. With three wetting agents and three different percentages of dye and wetting agent

concentrations there were twenty-seven combinations of solutions.

pH values from 3.5, the usual pH of the fruit, to 7.0 in steps of 0.5 were used. Sodium bicarbonate, calcium carbonate or citric acid were used to adjust the dye-wetting agent solutions to the pH wanted. All readings were determined by a laboratory Model G of the Beckman pH meter. The solutions were adjusted, then heated to boiling and held fifteen minutes at that temperature to simulate the commercial process. The objective of the study of the pH on the stability of the Erythrosine and wetting agents solution was to determine the pH to keep the dye in solution.

Surface Tension:

The instrument used in measuring surface tension was of the Du Nouy form as shown in Illustration 1. The method consists of measuring the force necessary to pull a platinum ring of known diameter away from the surface of the liquid. As the ring is lifted from the surface, the force increases with the distance and passes through a maximum before pulling away from the surface. The maximum was recorded automatically by the torsion balance.

ILLUSTRATION 1

INSTRUMENT TO DETERMINE SURFACE TENSION

The surface tension was calculated by the following formula:

$$\gamma = P/4\pi R$$

where γ is the surface tension in dynes per centimeter and P is the acceleration of gravity times the observed mass, recorded on the balance, needed to detach the ring of radius R from the liquid.

The surface tension was determined before and after heating to see if heat, pH and concentration of the dye had any affect upon the wetting agent.

Measuring the color of the solution:

This study of the color was used to determine how the pH, wetting agent and heat affected the color of the Erythrosine dye solution. The colors of the adjusted pH solutions were compared against an unadjusted pH control solution. The Erythrosine dye solution follows the Beers-Lambert law. Therefore, the concentration is a logarithmic function of the percentage of incident mono-chromatic light that is transmitted. This being the case, if the pH did affect the dye solution, such as to precipitate a portion of it, the colorimetric analysis would determine it.

The readings, optical densities, were made on the A C Model of the Fisher Electrophotometer before and after the heating.

Wetting determination:

The "wetting ability" of wetting agents is commonly used to determine the comparative efficiencies of the solutions. This was put to practice in this experiment to determine which solutions of dye and wetting agent had the best wetting ability when the surface tension readings were nearly alike. It was used as a means of eliminating solutions not needed. Since the "wetting ability of a product is a function of its concentration, it may be utilized to determine its concentration in the processing solutions. This was of particular interest because concentration may have to be kept within certain defined limits.

The test, Schwartz and Perry (13), consists of measuring the sinking time of a one inch diameter number six canvas disc under definite conditions of temperature, concentration of wetting agent and hydrogen ion concentration.

The number six canvas was chosen for this work for several reasons. A coarser variety of canvas is

too difficult to wet and too much time is required to conduct the test. A finer weave of canvas is too easily wetted and does not provide sufficient differentiation between products. The choice of number six canvas gave a balance between time saving and testing efficiency.

Measuring dye diffusion:

A method for determining quantities of the dye which had diffused into the cherry tissue presented a problem. Numerous references are cited on the separation and identification of coal tar dyes, but none was found on the extraction and quantitative measurement of the dye. Winton (19) and Jacobs (7) referred to the stripping of dyes from food by soaking them in alcohol or ammonia. After repeated trials it was found that the dye was extracted best from the food by soaking it in hot ammonia water.

After determining the proper concentration of ammonia, the following procedure was set up. Remove a definite amount of cherries at a specified time interval, cut into half and remove the adhering solution. Weigh twelve grams and then place into a small Waring blender. Add three ml of 4 N ammonium hydroxide,

100 ml boiling water and then blend for one minute. Pour into a 400 ml beaker. Rinse blender with 20 ml of boiling water and pour into the same beaker. Allow to stand thirty minutes with occasional stirring. At the end of thirty minutes, time schedule is very important for duplication, vacuum filter using number 7 Whatman paper. Remove filtrate and read electrophotometricly. This was repeated for four time periods of fifteen minutes, thirty minutes, fourty-five minutes and one hour; and the results compared.

Residual wetting agent:

The purpose of this determination was to measure any wetting agent which may have been left in the cherry tissue after the dyeing and rinsing. If an appreciable amount of the wetting agent was left as a residue, the process would probably have to be terminated, due to the possible accumulative effects on human metabolism.

Jones (9) developed a colorimeteric method for analyses of sulfonate residues. Jones found that sulfonated surface active compounds form colored salts with methylene blue giving the following reaction:

$$RSO_3^- \quad MB^+ = RSO_3MB$$

where RSO_3^- is the anion of the sulfonated wetting agent and MB^+ is the cation of methylene blue. These colored salts are soluble in chloroform and are quantitatively extracted from an aqueous solution without extraction of any uncombined methylene blue. The spectrophotometer was used to determine the concentration in the extract.

Testing Bleeding of Maraschino cherries:

This method was the same as outlined by Van Blaricom (16). The finished Maraschino cherry is placed into jars containing halves of pears. Sirup of 25° Brix and adjusted to pH of commercial cans of fruit cocktail, 3.8, was placed over the contents and then the jars were processed in water at 212° F for fifteen minutes. If bleeding occurred, it could be readily seen on the white pear tissue.

CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

Concentration of Dye solution:

The three concentrations of dye used were 0.04, 0.06 and 0.1 percent. It was concluded during the experiment that the 0.04 percent solution was not strong enough because it had only enough dye to give the cherry skin a very light shade of red. The other two solutions were of sufficient concentration to give the cherry the desired color. In using, those who are desirous of a darker shade of red should use the 0.1 percent solution. However, the 0.06 percent solution gives the cherry a good color. There is a slight increase in surface tension with the higher concentration of dye, but the difference in penetrating power is almost negligible.

Selection of Wetting agent and Concentration:

The results of the surface tension measurements, which were used to determine the proper concentration of wetting agent to be used, are shown in Table 2. It was concluded from this table that the percentage of non-toxic wetting agent to be used was 0.025.

TABLE 2

Effect of pH on Surface Tension and Optical Density

Code	pH	Surface Tension	Optical Density	Code	pH	Surface Tension	Optical Density	Code	pH	Surface Tension	Optical Density
1-A-D	3.6	34.99	.065	1-B-D	3.4	35.58	.075	1-C-D	3.6	35.44	.255
	3.9	34.70	.076		4.0	35.30	.105		4.2	34.72	.300
	4.4	34.60	.122		4.5	35.85	.130		4.5	35.25	.340
	4.9	31.66	.415		4.9	33.17	.360		4.9	32.79	.400
	5.4	32.06	.400		5.4	32.85	.360		5.4	32.66	.385
	5.9	31.14	.400		6.0	32.98	.372		6.0	32.62	.385
	7.1	30.87	.395		7.0	32.24	.380		6.7	32.13	.354
	5.9*	32.91	.415		6.0*	-	.380		6.2*	-	.400
1-A-F	3.6	36.91	.050	1-B-E	3.4	37.20	.170	1-C-E	3.3	35.60	.245
	3.9	35.95	.073		4.2	37.59	.200		4.1	36.48	.315
	4.5	37.92	.084		4.6	38.05	.250		4.4	36.32	.346
	5.1	31.48	.505		4.9	32.63	.395		4.9	32.74	.500
	5.5	30.47	.495		5.5	32.67	.430		5.3	32.50	.500
	6.0	33.87	.505		5.9	34.12	.500		6.0	32.75	.520
	6.9	31.72	.465		7.0	31.66	.470		7.0	32.36	.510
	5.9*	33.74	.517		5.9*	-	.500		6.3*	-	.525
1-A-E	3.4	39.64	.215	1-B-F	3.7	40.87	.340	1-C-F	3.6	36.55	.470
	4.0	37.79	.168		4.0	38.33	.360		4.1	35.43	.535
	4.5	35.90	.320		4.5	39.30	.450		4.5	34.62	.650
	4.8	31.80	.660		4.9	32.56	.660		4.9	32.76	.695
	5.4	32.67	.700		5.4	32.39	.680		5.4	33.42	.680
	6.0	34.58	.730		6.1	34.03	.710		5.9	32.48	.690
	6.9	34.10	.710		7.0	32.08	.695		6.9	31.97	.695
	5.9*	-	.712		6.0*	-	.710		6.3*	-	.745

TABLE 2 (CONTINUED)

Code	pH	Surface Tension	Optical Density	Code	pH	Surface Tension	Optical Density	Code	pH	Surface Tension	Optical Density
2-A-D	3.7	40.40	.075	2-B-D	3.6	37.13	.340	2-C-D	3.4	34.71	.215
	4.0	39.45	.185		4.0	36.40	.365		4.1	35.42	.395
	4.4	39.73	.375		4.4	34.65	.365		4.3	33.38	.355
	5.0	38.92	.380		5.0	35.49	.390		4.7	33.77	.375
	5.5	38.25	.395		5.5	35.13	.375		5.5	34.46	.385
	6.1	38.07	.365		6.1	34.10	.380		6.1	34.47	.400
	7.1	37.15	.400		7.1	32.73	.395		7.0	32.43	.390
	6.0*	-	.395		6.3*	-	.395		5.9*	-	.400
2-A-E	3.7	42.35	.100	2-B-E	3.6	37.72	.160	2-C-E	3.6	35.37	.080
	4.1	42.18	.160		4.0	37.13	.140		4.1	35.16	.150
	4.4	39.69	.450		4.4	35.17	.500		4.4	33.74	.460
	5.0	38.89	.495		4.9	35.05	.530		5.0	33.81	.520
	5.5	38.26	.490		5.5	34.40	.535		5.5	34.34	.530
	6.1	37.22	.450		6.1	34.65	.535		6.0	34.38	.525
	7.0	36.23	.490		7.1	33.67	.535		7.0	32.30	.540
	6.1*	-	.510		6.2*	-	.555		6.0*	-	.540
2-A-F	3.6	44.66	.155	2-B-F	3.7	38.90	.200	2-C-F	3.6	44.66	.130
	4.0	43.38	.290		4.1	37.48	.100		4.0	43.66	.170
	4.5	41.27	.300		4.4	35.23	.660		4.5	41.27	.730
	5.0	36.21	.670		4.9	34.07	.675		5.0	36.21	.745
	5.5	37.95	.680		5.5	34.07	.710		5.5	37.95	.740
	6.1	39.39	.680		6.1	33.61	.690		6.1	39.39	.710
	7.0	38.91	.710		7.0	32.28	.720		7.0	38.91	.750
	6.3*	-	.710		6.5*	-	.740		6.3*	-	-

TABLE 2 (CONTINUED)

Code	pH	Surface Tension	Optical Density	Code	pH	Surface Tension	Optical Density	Code	pH	Surface Tension	Optical Density
3-A-D	3.8	47.21	.100	3-B-D	3.7	41.00	.120	3-C-D	3.8	38.76	.170
	4.2	46.49	.250		4.2	41.00	.110		4.2	37.72	.210
	4.6	42.57	.390		4.7	38.72	.400		4.6	36.05	.385
	5.1	43.21	.410		5.1	36.49	.390		5.1	35.42	.410
	5.6	42.90	.405		5.6	36.54	.420		5.6	33.73	.390
	6.1	42.21	.410		6.1	36.24	.390		6.0	35.26	.410
	7.1	39.71	.405		7.0	34.00	.385		7.0	-	.395
	5.8*	-	.405		5.6*	-	.420		5.6	-	.395
3-A-E	3.7	47.38	.110	3-B-E	3.8	42.07	.140	3-C-E	3.9	39.48	.160
	4.3	47.21	.390		4.3	40.10	.280		4.8	39.43	.220
	4.6	43.87	.500		4.7	38.17	.520		4.6	36.21	.520
	5.1	42.72	.520		5.1	36.59	.475		5.0	35.68	.500
	5.6	42.75	.530		5.5	36.37	.515		5.6	35.04	.520
	6.1	42.86	.570		6.1	36.58	.515		6.1	34.24	.520
	7.1	37.71	.490		7.0	35.90	.520		7.0	32.76	.520
	6.0*	-	.535		5.8*	-	.550		5.7	-	.520
3-A-F	3.9	48.97	.170	3-B-F	3.9	43.80	.170	3-C-F	4.0	40.69	.170
	4.3	47.85	.390		4.6	42.49	.620		4.5	39.35	.430
	4.7	44.36	.725		4.7	39.11	.730		4.8	35.50	.680
	5.1	43.92	.720		5.1	37.43	.710		5.1	34.37	.685
	5.6	42.99	.750		5.5	36.85	.740		5.6	33.75	.680
	6.1	41.86	.750		6.1	36.93	.710		6.1	33.62	.710
	7.1	38.82	.710		7.0	-	.760		7.0	32.28	.690
	6.1*	-	.740		6.0	-	.740		6.0	-	.710

TABLE 2

Code	pH	Surface Tension	Optical Density	Code	pH	Surface Tension	Optical Density	Code	pH	Surface Tension	Optical Density
0.04% Dye	4.0	72.16	.195	0.06% Dye	4.0	72.50	.290	0.1% Dye	4.0	72.42	.310
	4.4	72.50	.320		4.4	72.65	.540		4.6	72.59	.710
	4.9	72.52	.400		5.0	72.64	.520		5.0	71.77	.680
	6.0	72.12	.380		6.0	72.53	.510		6.0	72.03	.700
	7.0	72.21	.400		7.1	71.95	.540		7.0	72.01	.720
	6.5*	-	.430		6.3*	-	.550		6.6*	-	.765

* Control

Code Designation

1 - Nacconol N R
2 - D-40
3 - Aresket
A - 0.025% wetting agent
B - 0.05% wetting agent
C - 0.075% wetting agent
D - 0.04% Erythrosine dye
E - 0.06% Erythrosine dye
F - 0.1% Erythrosine dye

FIGURE 1

SURFACE TENSION OF D-40

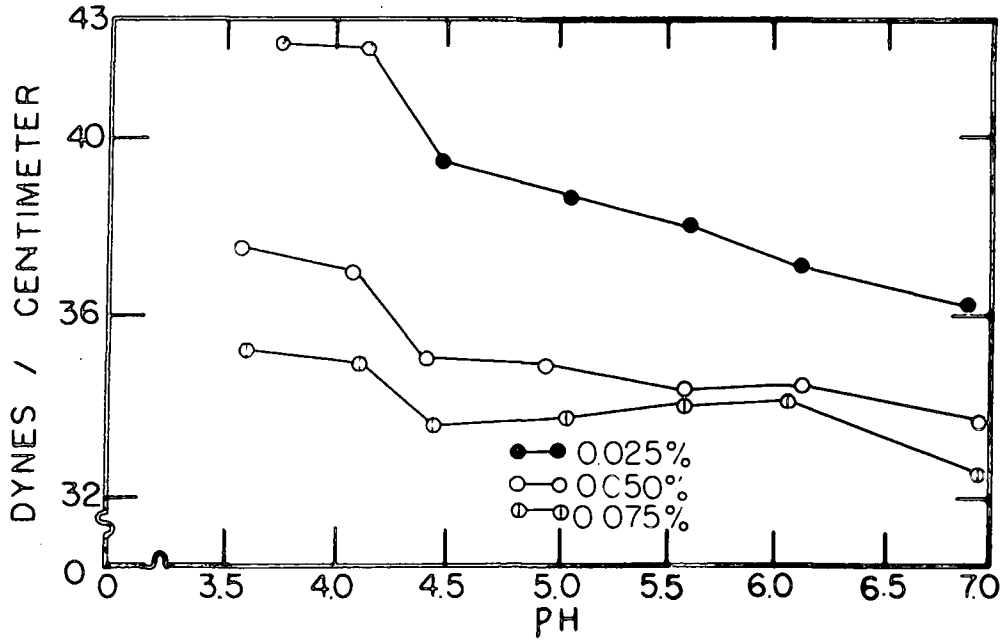


FIGURE 2

SURFACE TENSION OF NACCONOL NR

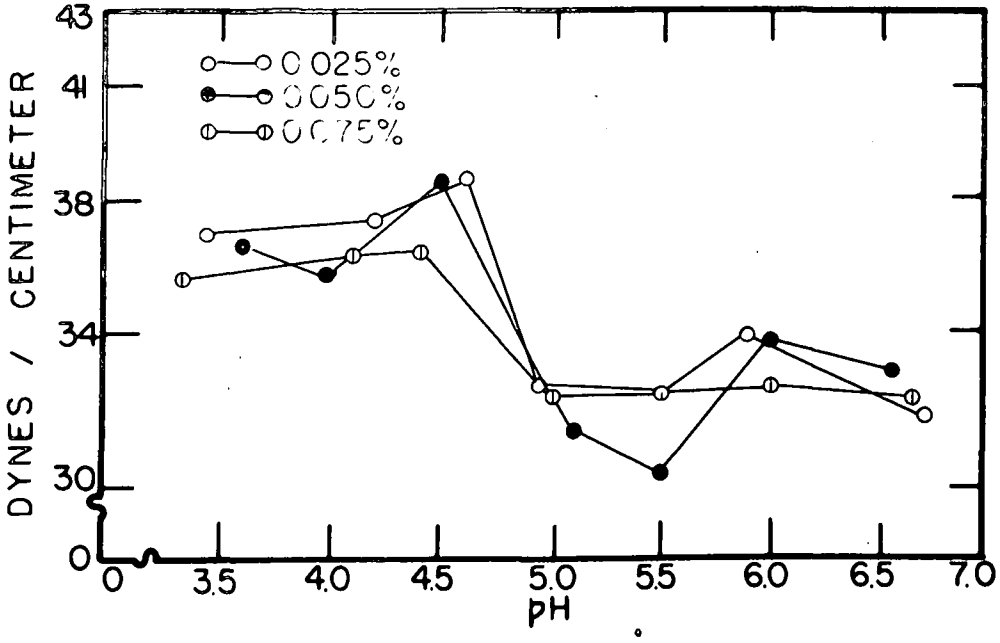


FIGURE 3

SURFACE TENSION OF ARESKET

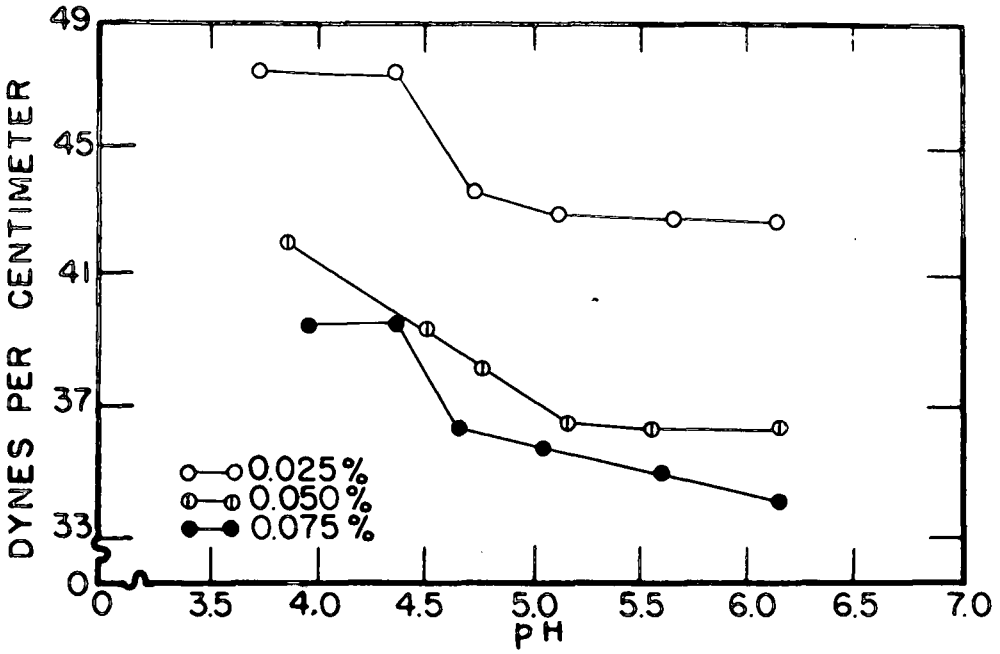
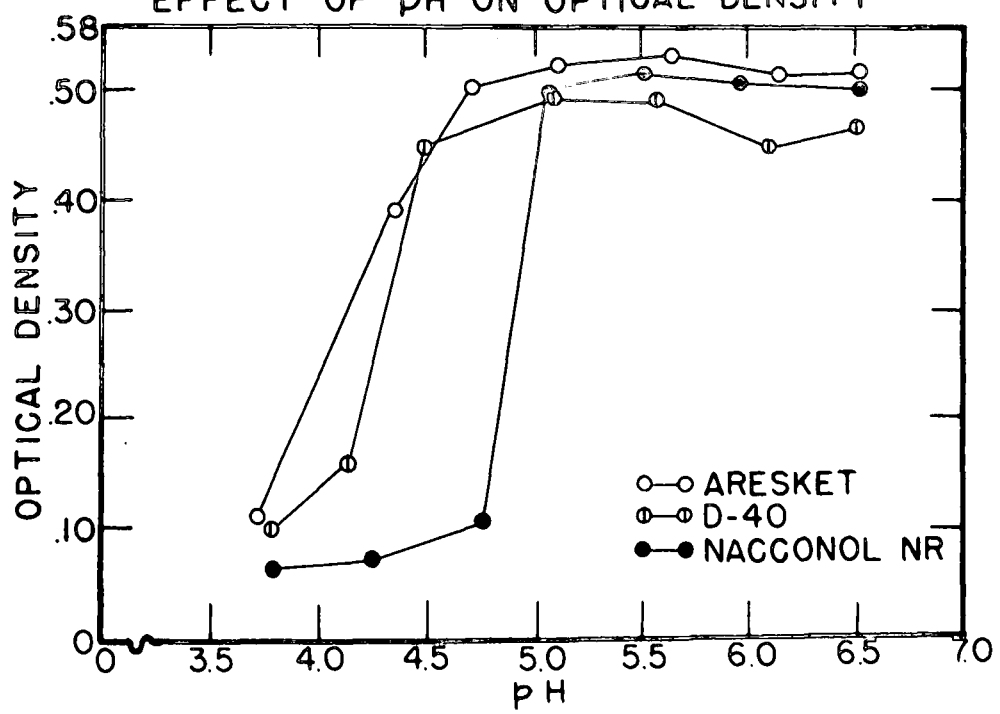


FIGURE 4

EFFECT OF pH ON OPTICAL DENSITY



Figures 1, 2, and 3, typical curves representing only one solution of each wetting agent, show that the 0.025 percent wetting agent in the Erythrosine dye solution reduced the surface tension values from 72 dynes per centimeter to approximately 43 dynes per centimeter. Thus, the surface tension was reduced to about half of its previous value and consequently a greater penetrating power is expected. These figures also show that the 0.05 and 0.075 percent concentration of wetting agent lowers the surface tension even more, but it was felt that the additional amount did not warrant any distinct advantages over the 0.025 percent solution.

With the selection of the 0.025 percent wetting agent in solutions of 0.06 and 0.1 percent dye strength, the problem was to determine which of the three wetting agents would give the best diffusion of the dye into the cherries.

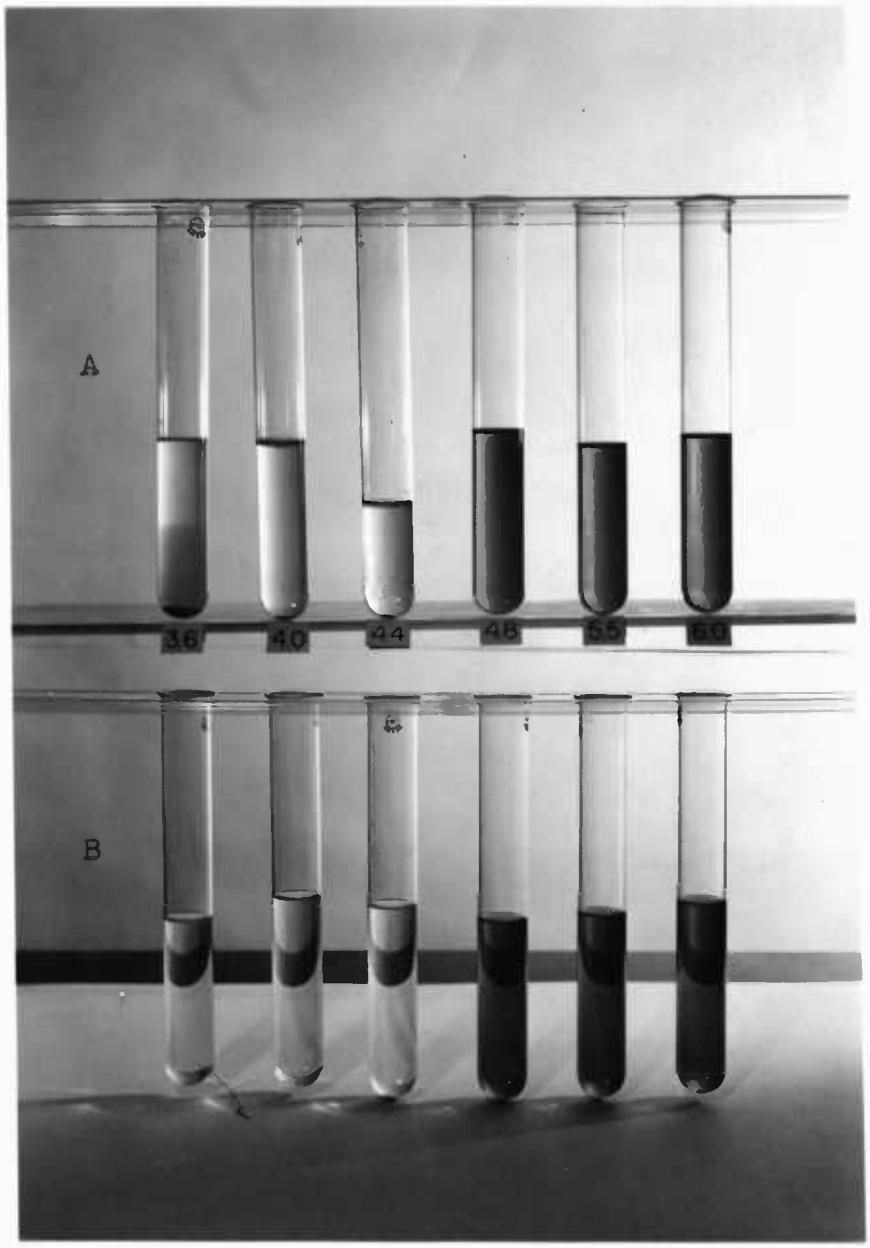
At this point the color determination was very useful to discriminate between the three wetting agents. The results of this determination, measured in optical density, are listed in Table 2. Figure 4 shows graphicaly only the results of the 0.025 percent wetting agents in the 0.06 percent Erythrosine solution. The optical

density values of the Nacconol N R solutions did not reach values comperable with the control until a pH of 5.0 or above. This was sufficient evidence to eliminate it from possible use because of the instability of the dye solution at pH 5.0 or below. The reason the optical density values are lower for low pH's than the unadjusted pH control value is that the Erythrosine dye was precipitated from the solution. Illustration 2 is an example of what happens when the pH is too low. These samples had been held for four months and the fine precipitate had time to completely settle. Since the solutions of D-40 and Aresket were stable in the pH range that is needed to process the cherries and they have approximately the same surface tension values, further work was conducted to establish which one of these should be used in the diffusion tests.

The method chosen was the Canvas Disk Wetting determination as described in the Experimental Procedures. The results are shown in Table 3 and it was concluded that the D-40 had better wetting properties than Aresket. The values for Aresket and the dyo were not exactly determined since the results were considerably higher than that of D-40.

ILLUSTRATION 2

THE EFFECT OF pH ON THE STABILITY OF THE ERYTHROSINE DYE SOLUTIONS



A - Two hours

B - Four months

TABLE 3

Canvas Disk Test

Trial	D-40 2-A-E	D-40 2-A-F	Aresket 3-A-E	Aresket 3-A-F	Dye only 0.06%	Dye only 0.1%
1	118	152	695	>600	>600	>600
2	95	150	>600	>600	>600	>600
3	101	124	>600	>600		
4	98	140	653	>600		
Mean	103	141.5	>600	>600	>600	>600

All results in seconds

Heating the solutions had only the affect of speeding up the precipitation of the dye in solutions with a lower pH than 5.0. In solutions with pH values above 5.0 there was not any distinguishable change.

Effects of pH:

Figures 1, 2 and 3 give the surface tension values and how they are affected by pH. Previously it was stated that the higher the concentrations of dye the higher the surface tension values. In these Figures the high surface tension (the low pH solutions) is due to precipitation of the dye as reported above, thus yielding a lower concentration of dye. Actually these are not contradicting statements but are borne out by the curve of Schwartz and Perry (13) which is characterized by a sharp initial decrease of surface

tension to a minimum, followed by a sharp short rise and then a further flattening out as the dye concentration is increased. When some of the dye had precipitated it is represented by the initial decrease while the higher concentrations are represented by the sharp rise and flattening out portion of the curve.

In all cases, there is a sharp lowering of surface tension at the pH where the solutions are stable. It is at values less than this pH that the dye can be set into the cherry tissue. When the pH was increased above this stable position the surface tension values remained fairly constant.

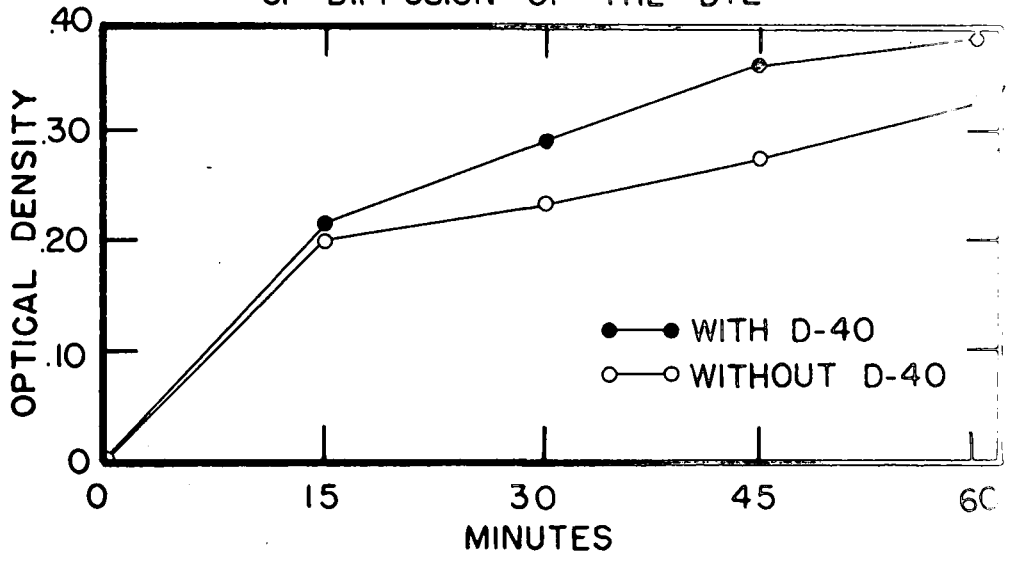
The colorimeter determinations show the same general trend with the effect of pH on the character of the dye solution. The solutions at low pH's have lower values due to the dye that has precipitated. The solutions at a higher pH, approximately 5 depending upon the dye-wetting agent combination, give readings of approximately the same magnitude.

Rate of Diffusion of the Dye:

With the procedure adopted, the rate of diffusion was determined at pH's of 4.6, 4.8, 8.5, 8.6 and 8.8. Figure 5 is a representative graph showing one group

FIGURE 5

EFFECT OF WETTING AGENT ON RATE OF DIFFUSION OF THE DYE



of results in Table 4. The results show a very distinct advantage of using the wetting agent in the preparation of Maraschino cherries because in all cases the dye had diffused faster into the cherry, no matter what pH was used.

The method using the non-toxic wetting agent saved considerable time in dyeing. Optical density readings obtained in one hour by not using the wetting agent were reached in only 38 to 45 minutes by using the wetting agent.

Statistical methods were applied to the results and it was concluded that the treated cherries have significantly higher values than the untreated ones and that this relationship is not affected by the pH value.[1]

Figure 6 shows the effect of the different pH treatments on the diffusion of the dye. Since there were not enough samples from each pH level, the lower ones were pooled together and the higher ones pooled in another group to determine statisticaly if pH showed a definite advantage. The results showed for this small sampling that the dye diffused significantly faster at the lower pH levels.

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1. Courtesy of Dr. Jerome Li, Biometrican, Oregon Agriculture Experimental Station.

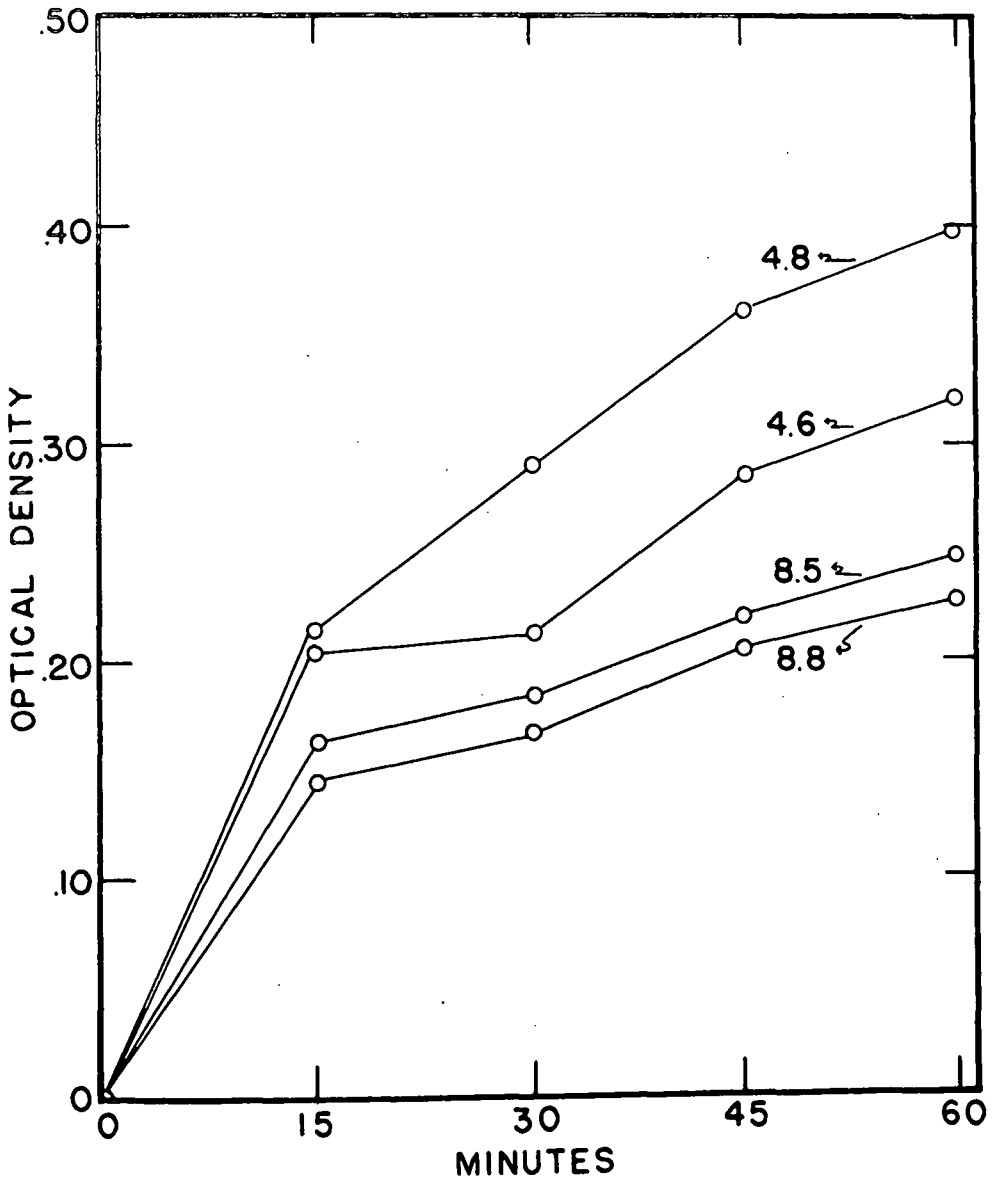
TABLE 4

RATE OF DIFFUSION OF ERYTHROSINE DYE

pH	Treatment	Optical Density 15 min	30 min	45 min	60 min
4.6	With D-40	.205	.222	.285	.324
	Without D-40	.180	.227	.260	.275
4.6	With D-40	.192	.217	.278	.320
	Without D-40	.172	.210	.242	.257
4.8	With D-40	.235	.315	.332	.372
	Without D-40	.218	.290	.298	.325
4.8	With D-40	.220	.290	.335	.355
	Without D-40	.180	.225	.272	.330
4.8	With D-40	.215	.290	.362	.398
	Without D-40	.205	.235	.278	.328
8.5	With D-40	.162	.185	.220	.248
	Without D-40	.145	.168	.182	.198
8.5	With D-40	.158	.175	.205	.225
	Without D-40	.145	.160	.180	.198
8.6	With D-40	.160	.180	.202	.225
	Without D-40	.148	.162	.182	.198
8.8	With D-40	.162	.180	.208	.228
	Without D-40	.152	.162	.192	.206

FIGURE 6

EFFECT OF pH ON RATE OF DIFFUSION OF THE DYE



Residual Wetting Agent:

The amount of residual wetting agent remaining in the Maraschino cherry is practically nil. The residue result (1.2 ppm), obtained by using the Jones test, is in the range where the method is sensitive only. The method is not accurate because of interferring substances which include fatty acid soaps and possibly other material occurring naturally in fruit. This small amount of wetting agent should not affect bleeding.

Bleeding Test on Prepared Cherries:

From all appearances, there is not a noted difference on the white flesh of the pears between a Maraschino cherry prepared with a wetting agent and those prepared without one. A slight tinge of pink was noticed on both when the jars were removed from the boiling water. This could be one of two things. Either the residual dye was not completely washed off and out of the seed cavity, or the dye on the outside of the cherry had been peptized by the heat and diffused into the pear half, Von Blaricom (16).

CHAPTER V

SUMMARY AND CONCLUSION

Work was conducted to determine the rate of diffusion of Erythrosine dye in the preparation of Maraschino cherries, using a method developed by the writer. A small amount of a non-toxic wetting agent was introduced to lower the surface tension of the dyeing solution and thus increase the penetrating power. If the time of preparation could be reduced and at the same time produce a colored cherry which would not bleed, it would be beneficial to those concerned with Maraschino cherry preparation.

It was found that the concentration of dye should be in the range of 0.06 to 0.1 percent Erythrosine. Concentrations below 0.06 percent do not give enough color to the cherry and concentrations above 0.1 percent do not give any added attractiveness. Of the three concentrations of wetting agents used, the optimum one necessary to depress the surface tension and therefore to increase the penetrating power is 0.025 percent.

The small amount of wetting agent supressed the surface tension from 72 to approximately 40 dynes

per centimeter. The additional depressions caused by 0.05 and 0.075 percent wetting agent were disproportionate to the increased cost.

D-40 proved to be the best all around wetting agent in regard to surface tension depression and high optical density of dye-wetting agent at low pH's. Nacconol N R gave the lowest surface tension values but was not stable at pH's lower than 5.0. Aresket, while it was stable at low pH's, didn't depress the surface tension as much as the other two wetting agents.

The residual D-40 wetting agent was measured as 1.2 ppm. This negligible amount had no affect on the bleeding of the cherries when they were packed with pear halves.

The application of a wetting agent significantly increased the diffusion rate of the dye. The validity of the method was tested by statistical methods and it was concluded that extracts which removed dye from the treated cherries had higher values of optical density than the untreated. This was in the pH range of 4.6 to 8.8 which is the normal commercial pH range for processing Maraschino cherries.

By using the wetting agent, only 64 to 75 percent as much time was needed to dye cherries as when a wetting agent was not used.

The pH does have an affect on the diffusion of the dye into the cherries and the results show that the dye penetrates quicker at pH of 4.8 than at a pH range of 8.0 to 8.6. There is less softening of the cherry at the lower pH. The pH affects the stability of the dye and wetting agent solution and it is recommended that the solution should not be less than 4.5.

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