THE BEHAVIOR OF THE ANTHOCYAN PIGMENTS IN CANNING

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INTRODUCTION

Many fresh fruits owe a considerable part of their attractiveness and consequent popularity to the bright red and purple colors of the anthocyan pigments present in the skin or flesh. It is desirable that the canned products made from these fruits retain the same brightness and freshness of color seen in the raw material. In the case of strawberries, raspberries, and cherries the degree to which the canned product retains the brilliance of color of the fresh fruit largely determines the desirability of a variety for canning purposes.

Much difficulty is encountered in securing satisfactory preservation of the natural colors in these and in many other fruits when canned, especially when the canning is done in tin. As a means of preserving more of the original color, the canning industry has resorted to the use of cans specially prepared by coating the inside with a lacquer designed to prevent contact of the contents with the metal. While the lacquered can permits much better preservation of color, it has proved a serious disappointment in another respect, as rapid corrosion of the metal occurs at breaks in the coating, and perforation of the can takes place much earlier than when plain tin is used. In consequence, the canner is forced to choose between placing heavily pigmented materials in plain tin, thereby losing in appearance but gaining in length of time over which the product may be held before consumption, or in lacquered cans, thereby gaining in appearance of the product but decreasing the time which will elapse before loss from perforation occurs.

A rather careful search of the literature has failed to reveal any detailed studies of the behavior of the anthocyan pigments in the course of canning processes. Various authors have mentioned the fact that fading or partial destruction of these pigments occurs, but they have advanced no suggestions as to the causes for the changes. The fact that pink, violet, or purple discolorations sometimes occur in peaches, pears, and other fruits has also been noted, but no investigations of the causes of such discolorations appear to have been made. Various tentative explanations have been offered, among which over-processing is most frequently mentioned. Among other causes, the use of sunburned fruit (*8*),[2] of fruit grown in very hot localities (*10*), permitting fruit to become overheated during shipment and before processing (*8, 10*), variety and degree of ripeness (*6*), and failure to cool promptly after processing (*16*), have been suggested. It has therefore been quite generally recognized that violet or pink discolorations are of occasional and sporadic occurrence in various

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[2] Reference is made by number (italic) to "Literature cited," p. 130.

canned fruits, but the reasons for such discolorations are very imperfectly understood, and it does not appear to have been suggested that the anthocyan pigments may stand in causal relationship to many cases of discoloration of this type.

The very extensive investigations of the anthocyan pigments made by Willstätter and his students (*34, 36, 37*) have shown that a single pigment may exhibit colors ranging from red to violet according as it is present in the free condition or as a salt. These workers have presented considerable evidence to show that many of the anthocyans form complex salts with metals, resulting in alteration in color. Shibata, Shibata, and Kasiwagi (*32*) have shown that in a very large number of anthocyans extracted from the colored parts of plants the addition of a metal to the aqueous solution produces a shifting of the color toward the violet end of the spectrum, the degree of alteration in color depending upon the metal employed. With aluminum sulphate and stannous chloride the colors produced, regardless of the original color of the pigment solution, are described as violet-red, pink, indigo, or lilac. That is, the action of either of these metals resulted in the production of some degree of violet color as a consequence of partial or total conversion of the free pigment into the violet-colored metallic salt. Nikiforowsky (*27*) considers that the color reaction with aluminum chloride is a specific reaction for anthocyans which permits them to be distinguished from flavonols and tannins. It is therefore well established that anthocyans generally, regardless of the color of the free pigment, react with many metals with an accompanying alteration of color toward the violet end of the spectrum.

It will be shown in the present communication that the presence in the material of anthocyans which react with the metal of the can is responsible for the discolorations characteristic of many fruits when canned in tin, and that the reaction of the pigment with the metal of the can is also largely responsible for the corrosion and perforation so characteristic of many of the pigmented fruits.

ANTHOCYAN PIGMENTS IN RELATION TO PINK OR PURPLE DISCOLORATION

In a number of fruits the anthocyan color is localized chiefly in the skin, and as a consequence of peeling is not usually present in the canned material. This is the case with the peach, the canned fruit usually showing no red or purple color. Any pink or violet discoloration which develops in the material subsequent to canning is therefore considered abnormal and often results in the discarding of the fruit as unwholesome and possibly poisonous.

A rather general appearance of discoloration in peaches put up by home canning clubs occurred in 1924 over a limited area lying between Athens and Augusta, Ga. Nearly all peaches canned in tin developed some degree of color, ranging from light pink to deep purple. In consequence, canning in tin was suspended, the trouble being popularly attributed to some defect in the tin cans being used.

The situation was brought to the attention of the writers by L. V. Strasburger, a chemist representing one of the can-manufacturing companies, who had spent several weeks in the territory in an attempt to find means of eliminating the difficulty. Strasburger submitted a number of cans of material for examination, and described his experimental work in detail. He had employed a great variety of modifications in time and temperature of exhausting and of processing, in concentration of sirup used, and in degree of ripeness of fruit employed, but more or less purple discoloration was invariably present in his experimental packs. Substitution of hand peeling for lye peeling gave no better results. Tin cans from several different makers were employed, some of which had been left from a supply used with satisfactory results in previous years. No differences were noted, however, in the material in the different cans, color appearing in all in about the same degree. In glass, the fruit was in every case a perfectly normal, clear yellow color. As this suggested that the discoloration was produced by tin, Strasburger processed fruit in glass jars to which metallic tin or stannous chloride had been added. Discoloration identical with that occurring in cans resulted. At this point, Strasburger presented the case to the writers, stating his conclusion that the discoloration was due to a reaction of some constitutent of the fruit with the metal of the can, and asking their assistance in determining the exact nature of the trouble. A similar request was subsequently made by a number of canning club leaders and home demonstration agents. In consequence, the writers undertook to determine the class of compounds in the peach responsible for the trouble, subsequently expanding the work to include a considerable number of other fruits.

EXAMINATION OF PEACHES IN 1924

Material of the variety Belle of Georgia, canned by Strasburger at Athens, was subjected to careful examination upon its arrival at the laboratory. The riper pieces showed considerable bluish purple discoloration at the surface, and adhering bits of peel at the spray-burned tips were bluish in color. The firmer hard-green fruits were usually normal in color but occasionally were faintly violet. Purplish discoloration in some degree was evident in the stone cavity of almost every piece, but was much more pronounced in the riper fruits. The interior surfaces of the cans showed some corrosion but this was not excessive, being less than that found in standard commercial canned peaches purchased and opened for purposes of comparison. As it was noted that the discoloration apparently deepened in tint after the cans were opened, the fruit was emptied into shallow porcelain dishes and allowed to stand at room temperature overnight. The color was greatly intensified, the riper pieces becoming uniformly purple, while the liquid became so deeply purple as to appear almost black.

This condition recalled an observation made earlier in the season. In the course of a visit to some of the canning plants in the vicinity of Fort Valley, Ga., the writers had examined samples of unpeeled pie peaches showing a somewhat similar discoloration. The fruit, which was somewhat underripe, was merely washed with warm water after stoning, packed in the cans, and given the usual processing treatment. When some of these cans were opened it was observed that the bright red color of the skins had faded to a dull purple or muddy violet, and that the liquid in the can was a cloudy purple. This was recognized as an alteration of the skin pigments, and led the authors to suspect that the discoloration observed in the peeled fruit might be due to the same cause.

Analyses made in the Bureau of Chemistry showed that the tin content of the discolored fruit, while somewhat in excess of that usually present in peaches examined so soon after packing, was not greater than that usually found in commercially canned peaches six to nine months after canning. Consumption of large amounts of the material by the writers showed that it was without harmful effects.

Some experiments designed to test the hypothesis that the development of purple discoloration was due to alteration in the anthocyans of the fruit were made on August 29, 1924, employing Elberta peaches grown at Arlington Experiment Farm, Rosslyn, Va.

The fruit was separated into two lots, one of which was soft ripe, the other in prime canning condition. The fruit was peeled by hand, packed in No. 2 plain tin cans, given a light exhaust, and processed 15 minutes at 100° C. A part of the material was packed with distilled water, a part with 30 per cent sirup, and a part with 30 per cent sirup to which 1 per cent of sodium chloride had been added. All the material was normal in color when opened except for a very slight purpling in the stone cavity in the case of the riper fruits packed in water or in sirup to which salt had been added. No change in color occurred when the material was allowed to stand in air overnight. The peels and stones from the fruit were packed in cans separately, water added, and processed exactly like the fruit. On opening, the peels showed different degrees of purpling corresponding to the degree of ripeness. The most intense color developed in peels from the ripest fruit, and the color became very intense on standing in air. The stones were intensely purple when the cans were opened. Additions of sodium hydroxide and ammonia in different amounts prior to canning decreased the discoloration of peels somewhat but did not wholly prevent it, and the material became deeply discolored on prolonged standing in air. Control lots of peeled fruits, peels, and stones were processed in glass. The fruit was normal yellow in color, the stones and liquid deep cherry red, while the color of the peels largely disappeared, the liquid becoming light red.

A quantity of stones were cracked, the kernels removed, and kernels and broken bits of stone were added separately to cans of peeled peaches prior to processing. The fruit with kernels added was normal except for a slight cloudiness of the liquid; that with broken stones had a deep purple liquor and the pieces of fruit were dyed superficially with the color.

These experiments pointed definitely to the red pigment as responsible for the discoloration, but indicated that contact with tin and subsequent exposure to air was necessary for its maximum development. They indicated also that the degree of discoloration depended directly upon the pigment content of the material. In consequence, some seedling fruit having a very intense red color extending from the skin into the flesh was employed for further work. Flesh, peels, and stones processed in tin showed considerably greater purpling at opening than did the Elbertas, and on standing overnight in air the flesh became a royal purple.

An aqueous extract of the pigment of the stones was made by heating a quantity of stones in water at 90° to 100° C. for 15 minutes. This yielded a deep wine-red solution. Heating with granular tin or adding dilute stannous chloride to this solution resulted in change of the color to very dark purple. Addition of citric acid to give a final concentration of 1 per cent preserved the red with very little change, and smaller amounts retarded the change in color to a degree proportional to the concentration.

From these experiments it seemed clear that the anthocyans of the skin and stone were responsible for the discoloration, and, as the pigment of the peach has never been investigated, it appeared advisable to make at least a partial purification of a quantity of it for a further study of its properties.

SEPARATION OF THE PIGMENT

About 3 kilograms of broken peach pits from which the kernels had been removed were extracted five times with glacial acetic acid. The extract was concentrated to small volume at 40° C. under greatly reduced pressure. The pigment was precipitated as a heavy sirup by the addition of about 10 volumes of ether, and the precipitate was washed several times with ether. It was then saturated with NaCl and extracted with butyl alcohol, repeated extraction being necessary to remove the bulk of the pigment. The butyl alcohol was washed several times with saturated NaCl, followed by three washings with a small amount of distilled water. The butyl alcohol was then concentrated under reduced pressure at 40° and the alcohol allowed to evaporate further at room temperature. The larger part of the pigment was precipitated from the butyl alcohol by the addition of several volumes of ether, collected on a filter, washed repeatedly with ether, and dried over calcium oxide. No attempt was made to crystallize or further purify the bright red powder. Its solution in water was almost neutral and was deep red with a tinge of purple. When the solution was rendered faintly acid, the color became deep bright red. Ferric chloride in nearly neutral solution gave a bluish black color in dilute solutions and a bluish black precipitate in greater concentrations. When the solution was made slightly acid, ferric chloride gave a purplish color, deepening to black. The absence of tannins, which would give a green color in acid solution with ferric chloride, was therefore indicated.

When the nearly neutral solution was heated with granular tin metal, slight darkening occurred, but there was no appreciable alteration of the red color. An acidified solution heated with metallic tin gave a deep purple color. With increase in the acidity of the solution the purpling decreased, practically no change occurring in strongly acid solution. When stannous chloride was added to a neutral solution, a blue precipitate was obtained. If the solution was slightly acidified and stannous chloride added, it developed a purple color, and a purple precipitate was thrown down. With increasing degrees of acidity the purpling decreased, strongly acid solutions remaining red with a faint tinge of purple. Aluminum chloride threw down a greenish blue precipitate from neutral solution; in slightly acid solution no change in color occurred. Lead acetate gave a greenish blue coloration in neutral solutions, but was without apparent effect upon a solution acidified with acetic acid. Zinc chloride gave a green color in neutral solution, which returned immediately to red when the solution was made slightly acid.

From the results of this examination of the pigment it is apparent that the purple discoloration observed in peaches canned in tin is due to a reaction between the tin of the can and the anthocyan pigment present. It is possible that iron may be a contributing factor, as the pigment shows somewhat similar color reactions with salts of iron. The results also suggest that the acid relations are quite important, since the degree of acidity greatly modifies the intensity of the color.

The explanation of the fact that discoloration of the canned product is occasional and sporadic in its appearance, lies in the fact that the amount of the pigment developed in the fruit is determined by climatic conditions, hence varies considerably from year to year. In the district about Athens and Augusta, Ga., in which it was observed in 1924, the summer had been exceptionally hot and dry, with more than normal sunshine, and all varieties of peaches were unusually highly colored. In the Fort Valley district of Georgia the season of 1924 was close to normal in temperature and sunshine, and the commercial canners encountered little or no discoloration. The season of 1925 in the Fort Valley district was one of considerable excess of sunshine and rather high temperatures, and the fruit of all varieties showed exceptionally brilliant color. As a consequence, considerable violet or purple discoloration was observed in the commercial pack of several canneries in that district. It is clear that seasonal conditions determine the occurrence of the trouble by controlling the amount of anthocyan pigment developed in the fruit.

EXPERIMENTS WITH OTHER FRUITS

The work with the peach was considered as definitely establishing the fact that purple or violet discoloration of the canned product is due to a reaction of the anthocyan pigment of the fruit with the tin of the container. As somewhat similar discolorations had been observed by the writers in grape juices canned in tin, as well as in certain fruits, they were led to believe that the phenomenon might be of somewhat general occurrence in the more heavily pigmented fruits. In consequence, experiments were carried out with a considerable number of such fruits, including grapes, plums, red and black raspberries, blackberries, strawberries, cherries, mulberries, apples, fruits of Crataegus and Viburnum, Indian strawberries, and with beets and red cabbage. The results obtained with these materials will be briefly described. In all cases such an amount of material was prepared as permitted examination a few days after canning and again after six to nine months' storage.

GRAPES

Uhland, a greenish yellow variety, was canned both in glass and tin. The two lots were indistinguishable in appearance when opened, both being a dull grayish green. No change occurred on standing in air. Catawba and Rogers No. 13, both of which are red varieties, placed in plain tin cans and processed without exhausting, were, respectively, deep reddish purple and faintly purple when opened. On standing 48 hours in porcelain dishes the color of the liquid from tin containers became intensely purple and the flesh of the berries was dyed by it. In glass jars the color was a faint clear red which did not alter on exposure to the air. Four black grapes—Cloeta, Eumelan, Worden, and an unidentified variety—differed only in the intensity of the deep purple color developed in tin. In glass all were purplish red or brownish red, but when the liquid was removed and diluted with water it was seen to be a clear red with no suggestion of purple. Berries and skins of the deeply pigmented varieties were separated and processed separately in glass and tin. The berries in glass and tin were the same grayish green. Skins processed in glass were a deep wine red and neither skins nor liquid changed color on exposure to air. A portion of the wine-red liquid, when heated after the addition of a strip of tin foil, became light purple and on cooling deepened to intense purple. Skins in tin cans were a magnificient royal purple when opened, and the liquid drained from them, when added to the normally greenish gray pulps, stained them purple. When a few skins of one of the black varieties were added to a can of Uhland, the greenish yellow variety, before processing the fruit became a brownish purple.

After standing in storage 8 to 10 months, plain tin cans containing red or black grapes were intensely corroded. In the grapes canned without separating pulp and skins, the skins had faded to a dull buff color, but the flesh of the berries was dyed purple from the surface inward and broken berries were colored purple throughout. The liquid was distinctly purple and quite milky in appearance, apparently from the presence of hydrous stannous oxide. On exposure to air the milkiness increased and the purpling of both fruit and liquid became very intense.

The behavior of the grapes canned in tin is in many points identical with the disorder of wines known as blue casse. This condition is frequently encountered, especially by the French wine makers, in red or white wines which have been brought in contact with iron at some stage of the process of manufacture, usually in pressing. The trouble usually becomes apparent only after the wine is aerated, as in racking. In the case of a deep red wine, such as that made from Lenoir or other heavily pigmented grapes, the color gradually changes after racking through bluish red to dull violet, with a thin iridescent film at the surface. Ultimately a blue-black precipitate settles out, leaving the wine more or less altered in color. In white wines, the color changes pass through grayish or leaden shades to dull brown or brownish black. There is an enormous literature upon blue casse which will not be reviewed here. The essential facts thus far developed are that blue casse is the result of the presence of iron, either in the fruit or derived from the equipment employed in pressing and handling the juice, and that the iron combines with some constituent of the wine, subsequently producing abnormal color and going more or less completely out of solution upon exposure to air. It is significant that red and white wines, which may be made from the same variety of grapes, show differences in the colors developed. In the case of red wines, the fruit is crushed and fermentation is allowed to begin before pressing in order that a considerable part of the pigment of the skins may be brought into solution. In white wines, heavily pigmented varieties may be employed, but the grapes are pressed cold immediately after crushing, in order that the pigments may not be carried into the wine. The differences in color of the red and white wines which develop casse may be due to the fact that in the red wines iron reacts chiefly with the pigment in solution, while in white wines the reaction is mainly with tannins.

A somewhat similar condition has been noted by Donauer (*11*) in the manufacture of Concord grape juice. He states:

> Concord grape juice is changed considerably in color by copper and copper alloys and nickel. The color is entirely destroyed by zinc or iron. Tin turns the color to a violet. Aluminum and its alloys or silver-plated metal are very satisfactory for such grape juice as far as its color is concerned.

The writers have found that the juices of any deeply pigmented grapes such as Lenoir, Clevener, Concord, Clinton, and Eumelan, whether fresh or pasteurized, give immediate color reactions upon the addition of ferric chloride, stannous chloride, or aluminum chloride in the cold, or by heating with metallic iron or tin. Upon the addition of stannous chloride the color is immediately transformed to purple or violet, according as smaller or larger amounts of the chloride are added. When acid is added the color returns toward red, finally becoming indistinguishable from the original juice. With aluminum chloride the change of color is less pronounced and the amount of acid required to produce return of the original color is much less. Ferric chloride produces an intense purplish black coloration, but the original color returns if sufficient acid is added. It may be pointed out that an identical treatment is employed with red wines which have developed blue casse, as they are acidified with citric acid and aerated, which restores much of the original color. There can be little question that reaction of the anthocyans with metals is responsible alike for the alterations in color and unfermented juices, in pigment-containing wines, and in the entire fruits when the materials are permitted to come in contact with metal.

APPLES

Three varieties of apples were employed. Two of these, Hyslop and Small Red Siberian, are crab apples having intensely red coloration in the peel with white or light yellow flesh. The third, Baxter, in addition to having a deep red skin has the flesh more or less colored by red streaks extending inward almost to the core line. Small Red Siberian was canned whole in tin and in glass. In glass the red pigment dissolved in the water and gave a reddish solution, the fruits becoming clear yellow. In tin both fruit and liquid were faintly purple and became intensely purple on standing, the staining effect of the liquid upon the flesh being especially pronounced. The fruits of Hyslop were peeled by hand, the peels themselves being canned separately. The peeled fruit showed no change in the light yellow color during processing or after opening and exposing to air; peels and liquid become quite purple during processing and were deeply colored after overnight exposure to the air. The red striping in the flesh of Baxter faded almost completely in the material canned in glass; in the material in tin it went over to a rather faint purple which had diffused into the surrounding flesh. After 24 hours' exposure to the air, the color deepened to a decided purple in both liquid and flesh.

Crataegus Berries

Fruits of red haw processed 20 minutes in No. 2 cans had the color discharged, the fruits becoming bright yellow and the liquid very faintly red. On exposure to air the liquid became faintly reddish purple. In glass jars the fruit was yellow and the liquid clear, remaining unchanged after prolonged exposure to the air.

Viburnum Berries

Fruits of Viburnum sp. lost somewhat of their bright red color in processing and developed considerable purple on prolonged exposure to the air, but the development of the discoloration was much less rapid than in grapes, apples, or plums. Another sample of fruit which was greatly overmature and badly shrivelled, lost practically all color in processing and did not change to purple on standing.

Plums

Only one variety of plum, the Abundance, was used. The bright red-skinned fruits were canned whole. Both fruit and liquid were intensely purple when the cans were opened and the color deepened to purplish black, the change being more rapid than in any other of the various fruits tested.

Raspberries

Three varieties of raspberries were employed. These were the St. Regis, a variety having bright clear red fruits; the Cuthbert, a dark red; and an unnamed black variety closely resembling the wild black form. These were exhausted 2 minutes and processed 45 minutes at 85° C. In glass the St. Regis retained its bright red color. In tin it was very similar in appearance to the samples in glass when first opened but on exposure to air the liquid developed a reddish purple color, and the fruits above the liquid became a very dark purple.

The Cuthbert and the black variety were canned in both plain and enameled tin, with controls in glass. The Cuthbert in glass was a clear dark red. The fruit in enameled cans showed considerable fading of the original color and had a distinctly purplish tint when first opened. After exposure to the air it went over to a purplish red distinctly darker than that of the fruit in glass. The loss of color was much more pronounced in plain tin than in enameled cans, and there was more purple apparent on opening. On standing the color became dark purplish red like that of the enameled cans.

The black raspberry underwent very little change in color in glass. In enameled tins the color was only slightly less good than in glass, but had a faint purple tinge. In plain tin the original color was largely replaced by deep purplish red. On standing in air the fruit from both enameled and plain tins became so intensely purple as to appear almost black.

Oregon Evergreen Blackberry

The color in glass and in enameled tin was deep dark red, the latter having a purplish tinge which was not present in glass. This increased only very slightly after 24 hours in the air. In plain tin the original color was markedly faded and the liquid was purple and milky, probably from the presence of hydrous stannous oxide, as the metal was greatly etched. After standing overnight the liquid was purplish black, with milkiness still persisting. A similar condition was observed in strawberries, cherries, cranberries, raspberries, and mulberries.

Strawberries

The variety of strawberry used was the Klondike, the treatment employed being a 2-minute exhaust and a process of 30 minutes at 85° C. In glass and enameled tin the color faded to an unattractive brownish red, the fruit in cans having a purplish tinge not present in that in glass. In plain tin the color was a dirty brownish red and the liquid had a turbid, milky appearance, with slight purpling. Very little change in color occurred in fruit from either plain or enameled cans on standing overnight in shallow porcelain dishes.

In connection with another study in the laboratory, the writers had canned small experimental packs of about 220 selections and strains of strawberries representing most of the commercial varieties. In this work both plain and enameled cans were employed. Examination of this material eight months after its preparation shows a very wide range of behavior. The only generalization which appears to be justified is that the use of enameled cans in all cases contributes in some degree to preservation of the original color of the material. Varieties differ widely in their behavior. In some cases the original red color is replaced by varying shades of brown or brownish red, without suggestion of purpling either before or after exposure to the air. In other cases some degree of browning, varying from slight to extreme in the different varieties, was accompanied by discoloration which ranged from barely visible violet to intense purple, and which deepened more or less on contact with the air. In every case material in plain tin showed more loss of the original red, more browning, and greater purpling, in cases where purpling occurred, than in enameled tins.

Cherries

A number of varieties of cherry, so chosen as to include both sweet and sour and to give a considerable range in the amount of pigment in the fruit, were used. These included three varieties of sweet cherries (*Prunus avium*), Baumann May (Guigne de Mai), Napoleon (Royal Ann), and Meeker; three varieties of sour cherries (*P. cerasus*), Early Richmond, Montmorency, and St. Medard, and one hybrid between *P. avium* and *P. cerasus*, Nouvelle Royale. Each of these was preserved in both plain and enameled cans and in glass. The fruit was exhausted 2 minutes and processed 45 minutes at 85° C.

SWEET CHERRIES

Meeker is a light red fruit of very low acidity, Napoleon is a yellow-skinned variety having a red blush, low in acidity. Baumann May was decaying badly and consequently was picked while underripe; the fruit used was heavily blushed with red and was quite acid. The three varieties behaved precisely alike in that all trace of red was lost in processing in glass, the fruit becoming a clear bright yellow. The fruit in both enameled and plain tin was likewise a clear yellow when opened, but developed a pinkish purple tinge in the liquid after standing overnight. There was a moderate degree of corrosion in the plain tins after eight months' standing in storage in the laboratory.

SOUR CHERRIES

Of the fruits of this type, Early Richmond was somewhat underripe; hence was lighter in color and higher in acidity than the others. Montmorency was a deeper red and less acid, St. Medard was a uniform dark red from skin to stone and was only mildly acid. In all three the fruit processed in glass lost somewhat in brightness of color through diffusion of the pigments into the water, but the color was a clear red proportional in intensity to that of the fresh fruit and there was no pink or violet tint. In enameled cans after eight months' storage there was more intense color in all varieties than in glass, but there was considerable purpling in St. Medard. In plain tin, the fruit of all the varieties showed pronounced fading after 8 months. The liquid was a faint pinkish red with decided milkiness in Montmorency and Early Richmond and purplish red in St. Medard. After standing overnight in porcelain dishes both liquid and fruit were decidedly purple in all cases, intensely so in St. Medard. The contrast between the fruit in plain and that in enameled cans was very striking. Very slight purpling occurred in Montmorency and Early Richmond from enameled cans, although there was considerable in St. Medard. Two cans of Montmorency, one in plain and one in enameled tin, which were sealed and processed without previous exhausting, showed considerably more discoloration than the corresponding exhausted cans, while the unexhausted plain tin can had greater milkiness than the exhausted plain tin.

The hybrid cherry, Nouvelle Royale, was not fully ripe; hence was lighter in color and more acid than is typical of this variety. Fruit in glass faded to a faint pink, that in plain tin became almost colorless. Enameled cans preserved much more of the color than did glass. There was a faint purpling in plain tin after standing overnight and an almost imperceptible deepening of the color in the material from enameled cans.

MULBERRIES

Three strains of mulberries selected by the late Walter Van Fleet were employed. They differed very little in color, acidity, or physical character. Their behavior in canning was identical. The color in glass after eight months' storage was a deep, dark red, very little, if at all, different from the fresh fruit. In enameled tin the color was very well preserved but slight purpling was present. In plain tin the color was a deep bluish purple in both fruit and liquid and the cans were heavily corroded. After overnight exposure to air there was very little change in the material from enameled cans, but that from plain tin had become intensely bluish purple. The effect of enameled cans in preserving the original color of the fruit was nowhere more strikingly evident than in the mulberry.

Indian Strawberry

The Indian strawberry (*Duchesnea indica*) is bright scarlet in color, the pigment being confined to the surface of the fruit. Color is entirely lost during processing, both in glass and tin, the fruit becoming a dingy reddish brown, which does not change on opening and aeration.

Purple Cabbage

In glass, the pigment of purple cabbage is largely extracted by the water, forming a beautiful, clear wine-red solution and leaving the tissue faintly red. In plain tin both cabbage and liquid were reddish purple, which became more intense on opening. After 17 months' storage material in glass had not changed materially, while that in tin had become light brown, about the color of ordinary cooked cabbage, and the entire inner surface of the can was deep purple to purplish black in color, due in part to sulphide blackening and in part to precipitation of the purple pigment.

Beets

Considerable fading of color, but no purpling, occurs in beets both in glass and tin. No suggestion of purpling is evident on heating fresh beet with stannous chloride, but if sufficient alkali to neutralize be added and the material heated with stannous chloride, a bluish-purple color appears and is followed by the throwing down of a purplish-black precipitate.

Cranberry

In cranberries canned in water, the liquid and the fruit became a clear deep red. Fruit in enameled cans differed very little from that in glass, but there was a slight purpling on occasional berries and a faint purple tinge in the liquid. After standing over night there was slight deepening of the purple tint in both berries and liquid. In plain tin there was very marked shifting of color from red to purple when the cans were opened four days after processing, and the color began to deepen immediately upon exposure to air, becoming pronouncedly purple overnight. The broken berries browned considerably as a result of oxidation of tannin when the fruit was emptied into a dish, and as a consequence the color of the fruit after exposure to air was blackish purple, the surrounding liquid being dark purple.

Summary of Results

The results of these experiments with various fruits show that the appearance of different shades of pink, violet, or purple during processing in tin cans, followed by intensification of the purple color upon exposure to air, occurs in a wide variety of fruits having red or black-red anthocyan pigments present in skin or flesh. In no case does such discoloration occur in fruits known to be free of anthocyans, or in the colorless portions of anthocyan-containing fruits. In consequence, the appearance of some degree of alteration toward purple when the material is brought in contact with tin would appear to be a general and characteristic reaction of the anthocyan pigments, which will be encountered in canning or other manufacturing processes which involve contact of the material with tin.

When anthocyan-containing material which has been canned in plain tin is stored for six to nine months, the color upon opening is decidedly bleached as compared with like material opened a few days after canning. Material opened shortly after canning becomes strongly purple when exposed to the air for a few hours; that which has been canned for some months and which, consequently, has become bleached or faded, undergoes a return of the color toward that present immediately after processing, but this is accompanied by more intense purpling than occurs in material opened just after canning.

Kohman has stated that anthocyans are bleached with the tin of plain tin cans, but that the original color can be restored by exposure to the air (*18*). It must be said that the writers have found in this work that the color which develops on exposure to air is not the same as that originally present in the fresh fruit or that present in the material after processing in glass, but that there is a distinctly deeper color, due to the presence therein of more or less violet, converting the original clear red to purple. While in very acid fruits the alteration is less marked than in those of low acidity, it is usually sufficiently great to be observed when the container is opened, and can scarcely be overlooked after the material has remained a few hours in contact with the air.

CHEMISTRY OF THE ANTHOCYANS AS RELATED TO THEIR BEHAVIOR IN CANNING

In order to secure more information as to the mechanism of the discoloration, aqueous extracts of the various fruits employed in the experiments just described were prepared by boiling a quantity of the fruit with water, expressing and filtering the liquid, dividing into portions, and modifying the hydrogen-ion concentration by graduated additions of citric acid or sodium hydroxide. The degree of color change produced by treatment of the unaltered juice with stannous chloride, ferric chloride, and aluminum chloride could readily be compared with the effect of similar treatments upon the same extract after addition of acid or alkali.

THE GRAPE

The pigments of the grape have received considerable attention. Willstätter and Zollinger (*39*, *41*) have examined varieties of *Vitis vinifera*, and Anderson (*1*, *2*) and Anderson and Nabenhauer (*3*, *4*) have studied varieties representing *V. labrusca*, hybrids of *labrusca* with *aestivalis* and *vulpina*, and a hybrid containing strains of *vinifera*, *aestivalis*, and *rupestris*. The results of these investigators show that the pigments present in these varieties, representing most of the species from which cultivated grapes have been derived, are members of the delphinidin group, being either oenin (delphinidin dimethyl ether) or derivatives closely resembling oenin.

Of the seven varieties of grapes employed by the writers, the greenish yellow variety Uhland appears to contain no anthocyan pigment, as no violet or purple color developed when aqueous extracts were treated with stannous chloride, either with or without modification of the hydrogen-ion concentration. Extracts of the two red and four black varieties examined [3] differed only in the intensity of the color developed. Extracts of the red varieties became faintly purple, those of black varieties deeply purple. The color developed in partially neutralized extracts was in all cases much more intensely purple. In acidified extracts the change became less and less marked with increasing acidity. It is to be expected that members of the delphinidin group of the anthocyans will show the color reaction here described, wherever they may be found.

The Cherry

Keracyanin, the coloring matter of the sweet cherry, *Prunus avium*, has been studied in a preliminary way by Willstätter and Zollinger. Its properties in so far as known appear to identify it with the cyanidin group of anthocyans (*40*). It appears to be partially converted into colorless form by heat, whether in presence or absence of tin metal or salts.

Aqueous extracts of both sweet and sour varieties of cherries were tested with stannous chloride, aluminum chloride, and ferric chloride. The purpling with stannous chloride or aluminum chloride and the blackening with ferric chloride were very intense in the extracts of the deeply pigmented sweet varieties, slight to moderate in those of the sour varieties. That the color change in the sour varieties is inhibited by the acidity of the extract is shown by the intense purple developed after partial neutralization. Upon the gradual addition of acid, the purple color developed with tin or aluminum or the blackening produced by iron progressively lessened, and sufficient acid restored the original clear wine red. As in other cases, the alternate addition of acid and alkali, with the resulting shift of color, might be continued indefinitely.

The Raspberry

The pigment of the raspberry has been assigned by Willstätter and Bolton (*35*), on the basis of qualitative reactions, to the cyanidin group. Their only statement with respect to it is, "Auch die Himbeere und die Frucht der Eberesche (Vogelbeere) enthält ein Cyanidinglucosid," no report of the tests being made. In its behavior with tin the pigment resembles those of other cyanin-containing fruits. Aqueous extracts of fresh raspberries, as well as juices from fruits preserved for one year by processing in glass, were examined. Addition of aluminum chloride produced no change in color. With stannous chloride there was slight purpling. On the addition of an alkali, the juice to which no metal had been added became greenish

[3] Uhland is a hybrid of *Vitis labrusca* with *V. riparia*. The two red varieties, Rogers No. 13 and Catawba, are *labrusca-vinifera* hybrids. Of the black varieties, Worden is pure *labrusca*, Eumelan a *labrusca-vinifera-aestivalis* hybrid, Cloeta a *lincecumii-rupestris-labrusca-vinifera* hybrid, while the parentage of the unidentified variety, which was employed by mistake for a named variety, is unknown.

black; that to which aluminum chloride had been added became distinctly purple; that with stannous chloride very deeply purple. By adding the alkali drop by drop, the color in the presence of either metal undergoes a progressive change from red with a barely perceptible tinge of violet on the addition of the first drop to intense purple as the neutral point is reached. When acid is added the original color, whether in presence or absence of metal, returns. By alternately adding acid and alkali the shift of color may be produced at will. This behavior is characteristic of both cyanin and delphinidin pigments encountered in this work. It would appear from the writer's observations that in order to secure the characteristic color reactions with metals, the acidity of the solution must be somewhat less in the case of cyanins than is necessary with delphinidins.

The Cranberry

The cranberry contains a cyanin pigment, idaein, which is a monogalactoside of cyanin (*38*). The juice of freshly cooked cranberries was found by the writers to give no change in color when stannous chloride or aluminum chloride was added. On bringing the juice nearly to neutrality either of these reagents produces a faint purpling followed by the deposition of a purple precipitate. Iron chloride produces little or no change in the freshly cooked juice, but on partial neutralization a brownish black color develops after a few minutes standing in air.

The Beet

Betanin, the pigment of the red beet, has been isolated by Schudel (*31*), who found it to be unique among anthocyan pigments in that the glucoside contained nitrogen to the extent of 8.6 per cent. It consequently appears that it does not belong to any one of the three groups of anthocyan pigments thus far established. This is significant, since very little alteration in the quality of the color was observed in the canning tests. The pigment apparently undergoes partial destruction or conversion to colorless form on heating, as considerable decrease in intensity of color occurs both in glass and tin. It does not show any purplish discoloration with metallic tin or stannous chloride after heating and exposure to the air. If fresh beets are sliced and cooked in presence of granular tin, the color is identical with that of controls cooked in distilled water. If cooked with granular tin and a little acetic acid, there is pronounced fading of color, and purpling at the surface of the liquid accompanied by formation of an iridescent film occurs on 48 hours' standing. If stannous chloride is added to the cooked beets and the solution is then neutralized, purple color develops, and a purplish black precipitate is thrown down from a faintly purple solution. The behavior of the pigment of beet with tin differs markedly from that of the pigment of the sweet cherry and of the grape.

The anthocyans of the other species included in this study have not been sufficiently studied with respect to their chemical composition to make it certain whether all of them are derivatives of pelargonidin, cyanidin, and delphinidin, singly or in mixture, or whether some of them are derivatives of yet other fundamental compounds. Detailed chemical investigation will be required to determine the nature of the pigment or pigments present in each case, since qualitative tests upon the crude pigments do not warrant the drawing of conclusions as to their chemical affinities, as Onslow (*28*) and Perkin and Everest (*29*) have pointed out.

The Strawberry

The strawberry material examined included more than 200 selections and strains representing a large number of varieties, and was of very widely differing character with respect to degree of acidity and amount of pigmentation. There was, consequently, no uniformity in behavior of the material canned in tin, as has already been stated. Material of Portia, a rather deeply colored berry, was employed in the tests of aqueous extracts with metals. It showed the same general behavior with respect to aluminum chloride, stannous chloride, and ferric chloride as the sour cherries. Addition of alkali intensified the purple color; addition of acid resulted in return to the original red. Material of Howard, a variety which contains a relatively small amount of pigment, was also employed. This berry faded in processing, even in glass, to dull brownish red. Juice of such material gave inconclusive results with stannous chloride and aluminum chloride, only a very faint purpling occurring with the former and none with the latter. The addition of acid caused the disappearance of the purple produced by tin salts, but the solution remained a dull brownish red with no intensification of the red. It is known from the work of Willstätter and his pupils that many anthocyans readily isomerize to colorless forms. It is also known that the presence of acids depresses or prevents the formation of the metallic compounds. In strawberries with a small amount of pigment and considerable acidity, isomerization, together with the browning of the tannins and the effects of the acid present, may be responsible for the difference in behavior from deeply pigmented forms, both in the can and in the presence of salts of tin and aluminum. The facts observed do not warrant the formation of an opinion as to the class of anthocyan pigments to which the color or colors of the strawberry belong.

Other Materials

In the other materials employed the color developed in tin was pink, pinkish red, purplish red, or purple, and in all cases intensification of the purple hue occurred when the material was left exposed to the air. The degree of alteration of color was in many cases clearly dependent upon the amount of pigment originally present in the fruit, faintly colored fruits giving faint pinks which deepened slowly to purple, as in the case of viburnum berries or light-red sour cherries. In Crataegus berries, the pigment is confined to the epidermal layers and is small in amount, and it is not clear whether the very slight purpling observed is due to partial destruction or decolorization of the pigment or merely to its small amount.

In the plum, raspberry, blackberry, mulberry, and red cabbage, the degree of alteration of color developed appears to be determined by the amount of pigment, but the resulting color is in every case some shade of purple. It ranges from rose red in the cranberry to a nearly pure violet in the mulberry, exposure to the air resulting in all cases in the intensification of the purple hue. With stannous chloride and aluminum chloride the same changes in color as described for grapes, peaches, and cherries were observed, and when acid and alkali were added the behavior was similar to that in these fruits.

It seems clear that pigments belonging to both the delphinidin and cyaninidin groups show the same general behavior in tin, and their aqueous solutions show color reactions of the same general character when treated with tin and aluminum salts, namely, a shifting of color toward violet with alkali and a return to red with acid. Minor differences in behavior have been noted. It is possible that there are differences in the readiness with which the reaction takes place, depending upon whether a cyanidin or a delphinidin pigment is concerned. There may also be differences between members of the same group depending upon the state of the pigment, whether free or existing as mono- or di-glucoside. In so far as the pigments of the fruits here dealt with are known, nothing has been observed which can be considered as a specific reaction for any particular pigment, or for any one of the various forms of combination in which the pigment is known to exist. The pigment of the red beet is an exception, its behavior differing markedly from that of the other materials examined.

The behavior of the anthocyan pigments of fruits and vegetables when canned in tin is in complete agreement with the results of Shibata, Shibata, and Kasiwagi (*32*). The writers have found that the effect of heating anthocyan-containing materials in a container having a coating of metallic tin, or in glass in presence of metallic tin, tin salts, or aluminum salts, is to produce some degree of modification of the original color toward purple in the case of every material tested, with the exception of those cases in which the pigment is totally converted to colorless form under heat. If the effect of the combination of anthocyans with metals is to bring about a shift of color toward the violet end of the spectrum, regardless of the chemical constitution of the particular pigment concerned, the uniformity of behavior observed in a variety of fruits having pigments of unknown chemical structure is readily understood.

METHODS OF PREVENTING OR MINIMIZING THE ALTERATION OF ANTHOCYAN PIGMENTS IN CANNING

The difficulty encountered in securing satisfactory preservation of color in many materials when canned in plain tin has led to the introduction and extensive use of the inside enameled or lacquered can. George W. Cobb (*9*) states that this type of can, originally developed in Europe for the canning of certain meats and fish, was first employed for colored fruits in America in 1902 and that its use for red fruits and beets had become quite general by 1905. Bitting in 1912 (*7*) recommended its use for raspberries, cherries, plums, beets, pumpkin, and hominy. Such texts as those of Cruess (*10*), Zavalla (*42*), and Powell (*30*) recommend the use of the enameled can for acid or highly colored products. Merriman (*24*) has discussed the origin and chemical composition of various lacquering materials and has pointed out the limitations of their usefulness.

Concurrently with the introduction and adoption of the enameled can the canning industry has sought to continue the use of the less expensive plain tin can for some of the colored fruits by selecting for canning purposes the more deeply pigmented varieties or strains, in the hope that a satisfactory degree of the original color might be retained when the material was preserved in plain tin. The results have been in part successful, in that a number of varieties of these fruits at present employed by canners can be put up in plain tin with a degree of preservation of color which makes them acceptable to consumers. In another respect the results have been disappointing. In the case of many fruits, the employment of the more heavily pigmented varieties of fruits results in more rapid generalized corrosion of the plain tin can or in more rapid pinholing of the enameled can than was encountered in the case of less deeply colored varieties of the same fruits. Attempts to increase the resistance of the can by modifications of the composition and methods of manufacture of the tin plate have been less fruitful than was hoped for (*6, 12–15, 25–26*). In consequence, the problem of corrosion and perforation is at present a more serious one than at any time in the history of the canning industry.

In the experiments here described, as well as in many others carried out in this laboratory in the past six or seven years, the anthocyan colors have in all cases been somewhat better preserved in enameled cans than in plain tin. In a few fruits, such as cranberries, the improvement due to the use of enameled containers, although distinct, is markedly less than in most materials. Even in the best enameled cans there is in all materials more loss of color than occurs in glass. Material canned in plain tin and opened a few days after processing shows considerable purpling and a milkiness of the liquid, neither of which is apparent in enameled cans of the same material opened after a like interval. When storage for six to nine months precedes the examination, considerable fading of the color is apparent in enameled cans, but is very much more pronounced in plain tin. On exposure to the air the material from plain tins undergoes marked intensification of color, finally approximating the purple tint observed on opening soon after processing. In enameled cans, some purpling occurs, but its amount is directly proportional to the area of metal exposed by imperfections in the lacquer.

ANTHOCYAN PIGMENTS IN RELATION TO CORROSION AND PERFORATION

The experience of canners with the various types of enameled cans and with plain tin as containers for the highly colored fruits and vegetables has led to recognition of the fact that the use of either involves difficulty. In the plain tin there is generalized corrosion of the inner surface with attendant loss of color on the part of the contents. In enameled cans there is better preservation of color but corrosion is localized at imperfections in the enamel, with the result that pinholing occurs in a relatively short time. In discussing this situation Baker (*5*) lists a number of fruits and vegetables which present especial difficulty. At the head of the list he places blackberries with strawberries next. The packing of these products he characterizes as gambling, not as a business. Rhubarb, blueberries, cranberries, black and red raspberries, loganberries, and blackberries are listed in the order of decreasing difficulty from the standpoint of perforation of cans. Baker recommends that those which are sufficiently deeply colored to endure the resulting loss of color, such as blueberries, cranberries, and black raspberries, be placed in plain tin to prolong the period prior to perforation. Others which are not so heavily pigmented may be placed in enameled cans to preserve the color and considered as perishable goods by reason of the certainty that perforation will sooner or later occur. In making this recommendation of the use of plain tin for materials of this character Baker has left entirely out of account one very important consideration, namely, that the continued action of the material upon the surface of the plain tin may result in such an extensive absorption of tin by the contents that the wholesomeness of the material will become questionable.

In the experiments with the pigments of various fruits described in the preceding section, it became evident that the acidity of the solution was a very important factor in determining the amount of change in color produced by the addition of metal. In highly acid solutions there is little color change for the reason that the formation of the metallic salt of anthocyan is depressed or inhibited. It might be inferred from this observation that in highly colored fruits, those of higher acidity would exert less corrosive effect upon the metal of the can than those of low acidity. For the purpose of studying the action of some of the anthocyan-containing fruits upon the container in relation to such factors as acidity, tannin content, and oxygen content, experimental packs of all the fruits examined with respect to behavior of their pigments with metals, together with a number of the nonpigmented materials, were canned in both plain and enameled cans. A part of the material was exhausted prior to sealing, a part sealed without exhaust. The cans were then stored for a comparative study of the amount of corrosion. A part of the material was opened at the end of six months, a part at the end of nine months, and the remainder was held for observation as to perforation. The study of this material brings out a number of facts in regard to the factors affecting rate of corrosion in pigmented fruits.

A comparison of exhausted and unexhausted cans six to nine months after canning shows very clearly that oxygen content is an important factor in promoting corrosion. In every case, regardless of the pigment content or of the acid content of the material, the cans which had not been exhausted showed more extensive corrosion than did the exhausted controls. This is in agreement with the work of Kohman and others. The results indicate also that the presence of oxygen, as in unexhausted cans, may in certain instances lessen the production of free hydrogen. They indicate also that the presence of oxygen, together with anthocyan, greatly accelerates corrosion; that is, the effect of the two factors is additive.

The results with pigmented fruits show considerable evidence that corrosion of the can is materially decreased by the presence of high acidity in the material. The highly acid cranberry attacks the metal of the can much less extensively than do sweet cherries, blueberries, mulberries, strawberries, and black raspberries, all of which are much lower in acidity. The highly acid Oregon Evergreen blackberry does not attack the can as vigorously as does the black raspberry. Whether acid content is the sole factor responsible for the marked differences observed in these cases can not be stated definitely, but certainly it is a factor. Oregon Evergreen blackberries and Logan blackberries combine high acidity and heavy pigmentation, but do not attack the cans to the extent that would be expected if the corrosive effect of these two factors were additive. In the cases just cited, and in a number of others encountered in this work, high acidity to a very considerable extent nullifies the corrosive action of the pigment, despite the fact that high acidity is itself a factor which increases corrosion. Rhubarb, for example, produces intense corrosion of the cans in which its acidity is an important factor. In those materials which are highly pigmented and at the same time highly acid, the acid depresses the formation of metallic salts of the pigment and thus decreases the rate and extent of the solution of metal. A considerable number of facts long on record in the literature without accompanying explanation become intelligible in the light of the experiments here described.

Studies carried out by Leach (*23, p. 623–625*) long since brought out the interesting fact that canned blueberries, having an acidity approximating one-twentieth normal, dissolved and carried into solution several times as much tin in a given time as strawberries or raspberries having twice the titratable acidity. Leach also tested various concentrations of malic, citric, and tartaric acids for their ability to dissolve tin from tin plate, finding that the pure tenth-normal acids dissolved only about one-tenth as much tin as did blueberries of one-half the acidity in equivalent time. The action of the pure acid ceased after about three months, no more tin being dissolved after nine months additional exposure. No such stoppage of action occurred in blueberries, which were nine times as efficient in dissolving the metal as canned tomatoes and twenty times as efficient as the pure acids. Leach could give no explanation of these facts, which are readily understood if we conceive of the anthocyan as continuously removing metal from combination with the acid and thus preventing the attainment of equilibrium between free acid and tin salt which occurs in pure acid solutions. It also explains results such as those of Donauer (*11*), who determined the rate of solution of metal of kettles used for Pasteurizing grape juice, concentrating apple juice, and cooking tomato pulp. The temperature for the grape juice was that of Pasteurization, while the other products were boiled down to an acid concentration somewhat exceeding that of the grape juice. The amounts of tin dissolved in equal periods of service bore the ratios, apple juice 80, tomato pulp 115, grape juice 380. The rôle of the anthocyan as a metal acceptor is here clear.

The reason why fruits of very low acid content but with large amounts of pigment, such as black cherries and blueberries, bring about more extensive corrosion of plain tin or earlier perforation of enameled tin than do more acid, less deeply colored fruits, such as red raspberries or sour cherries, is also clear. In the presence of large amounts of anthocyan, salts of tin with the acids of the fruits can have only momentary existence since they are immediately decomposed with transfer of the tin to combination with the anthocyan. In consequence there is sustained attack by the acid which may strip the tin completely from the steel plate, yet the amount of acid salts of tin present in the material will be very low. In fruits of high acidity and low anthocyan content the initial attack upon the metal is vigorous but the anthocyan is presently exhausted by combination with the tin, after which equilibrium between free acid and metallic salts is reached, and further action upon the metal ceases. The limiting factor in corrosion is not acid content, but anthocyan content, since the capacity for taking tin into stable organic combinations determines the extent to which it may be attacked.

PERFORATION

The material stored for the study of perforation was held at room temperature. The cans were in all cases stored on end, with the end which had been sealed after filling turned up. In all the experimental material, perforation was practically wholly confined to enameled cans. The percentage of hydrogen swells occurring in the enameled cans was also very much greater than in plain tin. In every case, enameled cans which ultimately showed perforation first became hydrogen swells. In only two cases did side perforations occur, in all others the perforation was located either in the countersink or at the juncture of the side seam with the end. In countersink perforations the opening is not at the bottom of the groove, but at the top, usually on the side next the center of the can. This is the region of maximum strain as a result of expansion during processing. The juncture of side seam and end seam is a region which is subjected to mechanical stress in the making of the cans, as well as to abrasion of the enamel covering. The location of perforations is therefore in accordance with expectation based on a knowledge of the behavior of metal previously subjected to strain when exposed to conditions favoring corrosion (*33*).

Packs of nonpigmented material prepared for comparison with pigmented material in the perforation studies gave no results since perforation failed to appear in such material.

It is apparent from the results of the author's comparative studies of the anthocyan-containing fruits that the amount of purple discoloration produced by contact with metal is a rather dependable indication of the ability of the material to perforate enameled cans. This holds true for the fruits of a considerable number of species which have been examined, and also for varieties and strains within a single species. Some 200 horticultural varieties and strains of strawberry have yielded evidence on this point. The most heavily pigmented varieties or strains were the first to perforate. Such deeply colored varieties as Portia and Progressive began to develop perforations after about six months, long before perforation began to occur in less highly pigmented varieties, such as Howard 17. The varieties of strawberries employed varied widely in acidity and in tannin content as well as in anthocyan content. The independent variations of acidity and tannin content complicate the results of the perforation study. Any substance which can take the dissolved metal out of combination with the acids of the fruit, thus setting the acid free to continue action upon the metal, will favor perforation or corrosion. Tannins and other substances capable of combining with the metal may function as aids to these processes just as anthocyans do. Consequently perforation, like corrosion, is favored by a variety of causes, of which the presence of anthocyan is only one.

The problem of discoloration is directly related only to such corrosion as is specifically due to the presence of anthocyans.

Kohman has given special attention to the problem of perforation by fruits containing anthocyans (*17–22*). He has shown that acidity of the fruit is not the most important factor determining perforation, since different products of like acidity but unlike pigment content show very large differences in the readiness with which they produce perforation. Kohman's results have led him to the belief that the rôle of anthocyan in perforation is that of a hydrogen acceptor—that is, the pigment takes up the hydrogen produced, so that perforation occurs without previous perceptible swelling of the can. The results obtained by the present writers indicate that anthocyan also functions as a metal acceptor, increasing the capacity of the material to dissolve metal by taking it into stable organic combination as rapidly as it is dissolved.

SUMMARY

Violet, pink, or purple discolorations in fruits and vegetables canned in tin are of rather widespread occurrence. In some materials such discolorations occur regularly, being accepted as a matter of course; in others their appearance is occasional and sporadic, resulting in considerable losses by causing the material to be discarded as unfit for food. Such discoloration has received various explanations, none of which are more than partially correct.

Discolorations of this type occur only in such fruits and vegetables as contain anthocyan pigments in skin or flesh, and are confined to the pigmented portions of the material. If pigmented and nonpigmented portions are separated prior to canning, discoloration appears in the pigmented portion but is absent from the nonpigmented portions.

The discoloration occurs only in material canned in tin, but occurs in both plain and enameled cans. When processing is carried out in glass, the original color of the material is preserved except for lessening in intensity due to partial conversion into colorless form by heat. In tin cans, a greater loss of color occurs, accompanied by conversion of some of the pigment to violet and consequent shifting of the color of the product toward purple. This alteration in color is intensified by opening the cans and exposing the material to the air.

The amount of anthocyan pigment developed in such fruits as have the pigmentation confined largely or wholly to the skin, as the red-skinned peaches, is determined in considerable degree by seasonal conditions. High temperatures and intense sunlight result in development of unusually high color in such fruits, and this results in the appearance of discoloration in the canned product.

The appearance of discoloration is due to the reaction of the anthocyan with tin dissolved from the container, and results in the formation of complex metallic compounds of anthocyan which are violet in color.

The anthocyan of the peach has been isolated and partially purified. Its behavior toward metals is similar to that of other anthocyan pigments.

The behavior of a large number of anthocyan-containing fruits and a few vegetables, including peaches, plums, sweet and sour cherries, apples, red and black raspberries, blackberries, currants,

grapes, mulberries, berries of Viburnum and Crataegus, red cabbage, and beets, has been studied by means of canning tests in plain and enameled tin and in glass; as well as the comparative behavior of aqueous solutions of the pigments with metals.

The formation of violet-colored salts with tin or tin salts is a general property of the red anthocyan pigments. It occurs when the anthocyan-containing material is heated in contact with tin, as in canning, when aqueous solutions of the crude or partially purified pigment are heated with metallic tin or aluminum, or when salts of these metals are added in the cold. The amount of the violet compound formed is determined by the amount of the pigment present, and by the degree of acidity of the medium, low acidity favoring its formation, high acidity depressing or suppressing it.

The color changes produced by combination with metals are reversible. Addition of alkali to a solution of pigment containing a metal results in formation of more salt with resulting intensification of violet color; addition of acid destroys the combination and restores the original red color.

In anthocyan-containing canned material the metal salts formed by combination of the acids of the fruit with the can metal are broken up by transfer of the metal into combination with the pigment, releasing the acid to continue attack upon the can. If the initial acidity is low, thereby favoring formation of the metal salt, extensive attack upon the can will occur, continuing up to the limit of the metal-absorbing capacity of the pigment. If the acidity is high, the formation of the metal-anthocyan compound is thereby reduced or suppressed, solution of the metal is limited to the absorbing capacity of the acids present, and equilibrium is reached before extensive corrosion occurs.

The enameled can preserves the original color of red fruits and reduces discoloration by decreasing the contact between pigment and metal. At the same time, it increases the rapidity with which perforations of the metal occur by limiting the area from which metal can be removed.

The processes resulting in discoloration are intimately related to the problem of corrosion and perforation, although these involve other factors. Anthocyan plays a very important rôle in causation of corrosion and perforation wherever it is present, but these processes can also be brought about by other compounds than anthocyans.

The principal factors concerned in corrosion are oxygen, acidity, anthocyan, and tannin. Some of these factors stand in antagonistic relationship. High acidity generally favors corrosion but depresses the formation of metal-anthocyan compounds and may thus retard corrosion. High acidity represses oxidation of tannin and formation of hydrous stannous oxide. Oxygen accelerates corrosion and increases the total activity by oxidizing the ferrous and stannous salts to the corresponding ferric and stannic states. The interrelationships of the factors concerned are so complex that practically every substance canned presents a specific problem.

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