THE HISTORY OF FOOD COLORANTS BEFORE ANILINE DYES

Harold T. McKone, Saint Joseph College

The addition of coloring agents to foods is not a recent phenomenon. In ancient Greece and Rome, wine was often artificially colored and inspectors were appointed to monitor this practice. In the first century A.D., Pliny the Elder comments on the Gallic wine industry as follows (1):

... about the rest of the wines grown in the Province of Narbonne no positive statement can be made, in as much as the dealers have set up a regular factory for the purpose and color them by means of smoke ... a dealer actually uses aloe for adulterating the flavor and color of his wines.

The first recorded “pure food laws” were passed in Europe in the early middle ages. A regulation concerning the adulteration of beer, enacted in 1292 in France stated (2):

Whoever put into beer baye, pimento, or “poix” resine was to be fined 20 francs ... for such things are neither good nor loyal to put into beer, for they are bad for the head and the body, for the healthy and the sick.

Butter was another commonly adulterated food. An Edict of Paris in 1396 prohibited its coloration with flowers, herbs or drugs. In England, bread appears to have been the most commonly adulterated food in the middle ages. As early as 1155, laws were passed regulating its composition, price, and formulation. Punishment for selling adulterated bread was severe (3):

If any default ... be found in the bread of a baker of the city, the first time, let him be drawn upon a hurdle from the Guildhall to his own house, through the greatest streets, where there are most people assembled, and through the streets which are most dirty, the false loaf hanging from his neck.

The great trade expansion of the 16th and 17th centuries brought tea, coffee, chocolate, and spices to Europe. With the influx of these new foods came more skillful methods of adulteration. Tea from China arrived with iron filings, clay, and gypsum to increase weight and mineral salts such as copper sulfate to intensify color. Joseph Addison (1672-1719) comments on the adulteration problem in England in 1710 as follows (4):

There is in this city a certain fraternity of chemical operators who work underground in holes, caverns, and dark retirements ... they can squeeze Bordeaux out of sloe and draw champagne from an apple.

The history of the coloring of tea in 18th century England is

References and Notes


William D. Williams is Professor of Chemistry at Harding University, Searcy, AR 72143. He collects and studies early American chemistry texts.
particularly interesting. It has already been mentioned that tea imported to England from China contained mineral salts for coloration. In addition, used tea was purchased from hotels and doctored with graphite to add weight and improve texture and with copper salts for coloration prior to repackaging and resale. This practice was so common that, during the reign of George I, a law was passed forbidding the addition of any substance to tea under a penalty of a £100 fine. This act was strengthened under George II in 1730. The preamble of this addition states (5):

...ill-disposed persons do frequently... color, stain, or dye such leaves and likewise mix tea with *terra japonica*, sugar, molasses, clay, logwood and other ingredients, and so sell and vend the same as true tea, to the prejudice of the health of His Majesty’s subjects, the diminution of the revenue, and the ruin of the fair trader.

In 1757, a tract entitled *Poison Detected* authored by “My Friend, a Physician”, was published. In this work, the author outlined how tea was colored by copper salts, veal whitened with chalk, beer adulterated with vitriol, and bread contaminated with alum, lime, chalk, and “sacks of old bones”. The millers who sold the flour to the bakers were the object of particularly harsh criticism (6):

Cannibals indeed let the body be dead before they devour it. But these savages of a more cruel and impetuous voracity, feast upon the living... our race of destroyers privily poison the food thru’ they prey upon us.

Another pamphlet, published almost simultaneously, “The Nature of Bread, Honestly and Dishonestly Made”, discussed the history of the adulteration of flour. The author, Dr. Joseph Manning, outlined the following procedure for detecting contaminants (including white lead) in bread (7):

Cut off the crust from a loaf, and setting it aside cut the crumb into very thin slices. Break these, but not very small, and put them into a glass cucurbit, with a large quantity of water... the crumb of the bread will in this time soften in all its parts. The alum will dissolve in the water and may be extracted from it in the usual way... the other ingredients being heavy will sink quite to the bottom... these (will be) the chalk, bone ashes, and whatever else was used.

To refute allegations of food adulteration, particularly of bread, a group of bakers published a reply in 1758, under the authorship of Emanuel Collins, entitled *Lying Detected*. Although these works added little insight into the growing
concern and controversy over food adulteration, they provided the foundation for what was to come.

Between 1780 and 1820, there was a definite increase in the incidences of the adulteration of foods with questionable colors. There are at least two reasons for this increase. First, during this time, there was widespread dissemination of trade handbooks and texts of secret recipes that outlined the methodology of adding colorants to foods. Secondly, this period marked the beginnings of modern chemistry. Thus, the color manufacturer and food trader could now have at their disposal a wealth of new chemical knowledge that could easily be applied to the adulteration of food. In 1798, Fredrick Accum (1769-1838), a German chemist living in London, published a series of articles in Nicholson's Journal entitled "An Attempt to Discover the Genuineness and Purity of Foods and Medicinal Preparations". This was the prelude to Accum's historic treatise on food adulteration, published in 1820. The full title being (8):

A Treatise on Adulterations of Food and Culinary Poisons, Exhibiting the Fraudulent Sophistications of Bread, Beer, Wine, Spirituous Liquors, Tea, Coffee, Cream, Confectionery, Vinegar, Mustard, Pepper, Cheese, Olive Oil, Pickles, and other Articles Employed in Domestic Economy, and Methods of Detecting Them.

The cover leaf of the book depicted a skull in a cup bordered by snakes with the caption "There is Death in the Pot" (a phrase taken from II Kings, 2:40). A most informative biography of Accum can be found in a series of articles by Browne (9-11).

In this master work, Accum not only described in great detail the effects of eating foods contaminated with poisons (including numerous colored mineral salts) but also provided names and addresses of merchants selling these products. The following three examples from Accum's work will help to illustrate the extent of food adulteration in England during the first half of the 19th century (8):

A gentleman who had occasion to reside for some time in a city in the West of England was one night seized with a distressing but indescribable pain in the region of the abdomen and of the stomach accompanied with a feeling of tension, which occasioned much restlessness, anxiety, repugnance to food... in 24 hours the symptoms entirely vanished. He had recollected that he had ordered a plate of toasted Gloucester cheese of which he had partaken heartedly and which, at home, he had regularly ate for supper. The landlady (of the inn) ordered the cheese to be examined by a chemist who reported that the cheese was contaminated with lead. It was found that the color of the cheese was heightened with red lead!

...Vegetable substances, preserved in a state called pickles, whose sale frequently depends greatly upon a fine lively green color, are sometimes intentionally colored by means of copper...numerous fatal consequences are known to have ensued...a young lady amused herself by eating pickles impregnated with copper. She soon complained of a pain in the stomach...in nine days after eating the pickle.
death relieved her of her suffering.

... The mode of preparation of ... (anchovy) fish sauce consists of rubbing down the broken anchovy in a mortar; and this triturated mass, being of dark brown color, receives, without much risk of detection, a certain quantity of Venetian Red ... adulterated with orange lead ... for the purpose of coloring it.

Accum prophetically warned against the use of these colors and listed foods most commonly adulterated with these poisons. Confectionery products were often contaminated with one or more of the following: red sulfuret of mercury (mercury sulfide), verdigris (copper acetate), blue vitriol (copper sulfate) sugar of lead (lead acetate), white lead (lead carbonate), and Scheele's green (copper arsenite). Accum's work attracted some attention in the United States which, up until this time, appears to have had little interest in the problem of food adulteration. An American edition of Accum's book was published by A. Small of Philadelphia in 1820.

In 1831, an article by William B. O'Shaughnessy (1809-1889), entitled “Poisoned Confectionary”, appeared in The Lancet (12). In this paper, the author discussed the composition of colored confectionery as well as the papers in which they were wrapped. Not surprisingly, the pigments found in the former included red oxide of lead, red sulfuret of mercury, and yellow chromate of lead. The wrapping paper, without exception, contained one or more of the following poisons: red sulfuret of mercury, yellow chromate of lead, or green carbonate of copper. O'Shaughnessy made the following plea (12):

It will scarcely be believed that the only enactments in the English code relating to public health ... are those which enforce the obser-

In spite of this plea, and of the serious concerns previously raised by Accum, there was no discernible government action in England to regulate food adulteration at this time. In fact, Accum's enemies (of which he had many) forced him to return to his native Germany in 1821 under what appears to be unproven charges of mutilating library books! The result was that food adulteration in England continued unabated for another 30 years.

On the continent, particularly in France, Belgium and Switzerland, food manufacturers had long been forbidden to use injurious color additives under severe penalties. As early as 1800, French law forbade the use of any mineral pigments in candy. Under the orders of the Préfet de Police of Paris, 10 December 1830, it is stated (13):

It is forbidden to wrap sweetmeats in paper glazed or colored with mineral substances. It is ordered that all confectioners, grocers, and dealers in liqueurs, bonbons, sweetmeats, lozenges, etc., shall have their name, address, and trade printed on the paper in which the above articles will be enveloped. All manufacturers and dealers are personally responsible for the accidents, which shall be traced to the liqueurs, bonbons, and other sweetmeats manufactured or sold by them.

In the early 1850s, in England, Dr. Arthur Hill Hassall...
(1817-1894), a physician, began a series of articles in The Lancet on food adulteration. These articles captured the imagination of the British public. In these papers and in his subsequent book (14) Hassall presented in great detail the extent of adulteration of foods, drugs and beverages.

The following bleak description of the plight of the British people at this time may help place the problem in perspective (15):

From morning to night he is the subject of perpetual fraud. He shaves himself with an inferior imitation of some high-priced soap; puts on a coat made of shoddy, and a hat of silk imitation of beaver. He drinks chicory and beans in his coffee, water in his milk, and organic matter of the vilest kinds, with the animalcules which are its scavengers, in the water itself. He may reasonably expect to be poisoned with his wines and liqueurs; but he is unsuspicuous that he is eating lard in his butter, alum in his bread, disgusting parasites, flour and gypsum in his sugar, meal in his mustard, turmeric in his ginger, sulphuric acid in his vinegar, lead in his cayenne, copper in his pickles, gelatine in his isinglass, potato-starch in his arrowroot, and many mineral poisons in bonbons and confectionery, or that his potted meats may be made of horseflesh his tea of used leaves revamped, his cigar falsified, and his bonbons and confectionery, or that his potted meats may be made of horseflesh. He drinks cocoa adulterated with meal and flour.

Like Accum, Hassall not only listed the mineral salts utilized as colorants, but also provided names and addresses of those responsible for selling these poisons. Hassall describes a candy pigeon cake ornament as follows (16):

The pigments employed for colouring the pigeon are light yellow for the beak, red for the eyes, and orange-yellow for the base or stand. The yellow colour consists of the light kind of CHROMATE OF LEAD, or PALE CHROME, for the eyes, BISULFURET OF MERCURY, or VERMILLION, and for the stand, the deeper variety of CHROMATE OF LEAD, or ORANGE CHROME.

Of the 101 samples of confectionery products analyzed by Hassall, 50 were colored with chromate of lead, 12 with red oxide of lead, six with bisulfuret of mercury, one with carbonate of copper, and nine with arsenite of copper. In several cases, there were as many as three or four poisons in a single sample. The human toxicity of these colors was well known at the time which makes it all the more unbelievable that their use was so widespread. As Hassall states (16):

The preparations of lead, mercury, copper and arsenic, are, what are termed cumulative - that is, liable to accumulate in the system little by little, until at length it becomes thoroughly impregnated or saturated with these poisons.

Hassall makes a particularly strong point in stating his concern that tainted confectionery is consumed primarily by children (16):

Table 1. Foods commonly adulterated with mineral colorants in the mid 19th century.

<table>
<thead>
<tr>
<th>Food</th>
<th>Coloring Agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colored confectionery</td>
<td>Arsenite or chloride of copper</td>
</tr>
<tr>
<td>Pickles, bottled fruit</td>
<td>Acetate or sulfate of copper</td>
</tr>
<tr>
<td>Custard powders</td>
<td>Chromate of lead</td>
</tr>
<tr>
<td>Cayenne &amp; curry powder</td>
<td>Red oxide of lead</td>
</tr>
<tr>
<td>Chocolate</td>
<td>Sulfide or red oxide of mercury</td>
</tr>
<tr>
<td>Butter</td>
<td>Carbonate or acetate of lead</td>
</tr>
<tr>
<td>Tea</td>
<td>Chromate of lead</td>
</tr>
</tbody>
</table>

The deadly poisons, like the above, should be daily used for the mere sake of imparting colour to articles of such general consumption as sugar confectionery - articles consumed chiefly by children, who from their delicate organization are much more susceptible than adults - is both surprising and lamentable. It is surprising, on the one hand, that the manufacturers of these articles should be so reckless as to employ them; and, on the other hand, that the authorities should tolerate their use.

In addition to candy, tea, cayenne powder and pepper were also commonly colored with mineral pigments at this time. Tea was often contaminated with iron sulfate, lead chromate, copper carbonate, copper arsenite, prussian blue and indigo. Tea seized by the authorities in London contained 35% copper carbonate by weight. Another sample in Manchester, England was found to be dyed with potassium chromate.

Cayenne and curry powder were adulterated with red oxide of lead, red sulfuret of mercury, and/or copper acetate to conceal other adulterations and to maintain a bright red color (since both of these spices lighten in sunlight). Gooseberries, rhubarb and olives were often colored with copper sulfate which also acted as a preservative. Hassall emphasized the extent of the problem in England in the middle of the 19th century as follows (14):

I had bought a bottle of preserved gooseberries ... and had had its contents transferred into a pie. It struck me that the gooseberries looked fearfully green when cooked ... after having ... mashed the gooseberries with a steel fork. I was about to convey some to my mouth when I observed the prongs to be completely coated with a thin film of bright metallic copper.

Even wine did not escape the adulterer's hand. Hassall notes that wine not infrequently contained lead. The source of this was lead acetate which was added to prevent souring, increase sweetness, and render muddy white wines clear. Hassall notes that "there is scarcely a country in Europe, except England, in which the employment of the poisonous pigments
in this report is not prohibited under the severest penalties" (16).

Partly as a response to these strong statements, Parliament appointed a committee to investigate the extent of food adulteration. They concluded that indeed, public health was endangered by these additives and passed the Adulteration of Food and Drink Act of 1869. This empowered “public analysts” to test foods submitted by local health authorities and by British citizens. Little by little, toxic mineral pigments were removed from foods and beverages in England.

Meanwhile in the United States, there appears to have been little organized opposition to the adulteration of foods and beverages until the 1850s. In 1859, an article appeared in Merchant Magazine on “adulterations in Foods and Drugs” which discussed a report in a Boston newspaper (The Boston Traveler) on the doctoring of foods with questionable additives (17). Foods commonly adulterated with poisonous mineral salts in the United States at this time are listed in Table 1.

During the mid-1800s, in the United States, it was virtually impossible to find any food, drink, or medicine that had escaped extensive contamination. Even cod liver oil was adulterated almost to substitution with train oil mixed with iodine. Yellow-tinged milk was so common that people refused to purchase white milk thinking that the latter had been doctored. The yellow tint in milk (often produced by the addition of lead chromate) was present to prevent detection of skimmed or watered milk, which has a blue hue.

In 1862 the North American Review printed an article outlining Hassall’s work that ended with the following plea (15):

In Massachusetts, we have very few restrictive laws on such subjects; and even these - as the laws relating to the weighing and stamping of bread, and sale of milk - are a dead letter and inoperative. When we see the difficulty of passing an effective law in England, as compared with the more positive and executive governments of the continent of Europe, we may form some idea as to the possibility of enacting prohibitory statutes against adulteration in this country, and of executing them afterward. There are few journals that have either the courage or the position and ability of the Lancet to expose these frauds; besides which, the result of such exposures can only be temporary. The best that can be done is to enlighten the public thoroughly and frequently as to what they are unconsciously suffering, through the press; and finally public opinion may take up the subject, and pass laws and enforce sufficient penalties. Until then, we fear that the defrauded consumer of adulterated foods can have as his only safeguard that insufficient maxim of jurisprudence, CAVEAT EMPTOR!

In 1856, the English chemist William Perkin (1838-1907) prepared the first synthetic dye, “aniline purple” or mauve, from coal tar. Within a few years, a variety of these organic dyes began to replace mineral pigments as food colorants. However, toxic inorganic salts continued to be used as food colors up to the turn of the century as can be seen from the following (18-19):

- In Boston, MA in 1880, 46% of candy sampled contained one or more mineral pigments, primarily lead chromate
- Well into the turn of the century, vermicelli manufacturers routinely added lead chromate to their product to provide the correct “egg-yellow” color
- It was common to color pickles and canned vegetables with copper sulfate until about 1905.

These conditions led inevitably to enactment in the United States of Federal laws prohibiting the coloration of foods and beverages with toxic mineral salts. In 1906, the Pure Food and Drug Act was signed by President Theodore Roosevelt (20). In this law, provision was made to certify food dyes by the Secretary of Agriculture, but, importantly, this certification was voluntary. This law, however, provided the foundation for the Federal Food, Drug, and Cosmetic Act of 1938 which made certification mandatory for the 15 aniline based food colors then on the list. Our present six certified artificial food colors are all derived from coal tar, rather than from inorganic minerals. Present government requirements for the certification and safety of these six food colors are the same as for the certification of all food additives and include premarket safety evaluation. Although some concerns are presently expressed over the safety of food additives in general and food colors in particular, we have come a long way from the pre-regulation era when lead, copper, mercury and arsenic salts were routinely added to almost every food and beverage in the marketplace.

References and Notes

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10. Ibid., pp. 1008-1034.
11. Ibid., pp. 1140-1149.

Harold T. McKone is Professor of Chemistry at Saint Joseph College, West Hartford, CT 06117 and is particularly interested in the history, chemistry and biochemistry of food additives.

EARLY INDUSTRIAL pH MEASUREMENT AND CONTROL

John T. Stock, University of Connecticut

Being used for sales pitches for cosmetics and the like, the term "pH" has become part of our everyday language. The importance of pH ("hydrogen ion concentration" in the older literature), and hence of its measurement and control, is therefore readily accepted.

Nowadays, the glass-electrode pH meter is a very common instrument. Although the glass electrode was described in 1909 (1), its high electrical resistance delayed its routine use until the development of suitable electronics nearly three decades later. Accordingly, pH measurements were made in the laboratory by the use of chemical indicators, or by low-resistance potentiometric indicators such as the hydrogen, antimony-antimony oxide, or quinhydrone electrodes (2).

Adaptations of these systems filled some important industrial needs until glass-electrode technology reached a state of maturity. For example, a rather complicated system for the control of water-softening by the lime-soda process was patented in 1906 (3). Dosing was regulated by photometrically monitoring the color change of phenolphthalein. Concerning potentiometric systems, the hydrogen electrode has a long and interesting history (4). One of its earliest industrial applications was to the estimation of the acidity of tanning liquors (5).

Earl A. Keeler was greatly involved in the development and use of the industrial hydrogen electrode. He was born in 1892, joined Leeds & Northrup in 1913, and remained with this instrument-making firm until the end of 1922. Judging by the gentle fun poked at him by the editor of the firm’s house journal *The Recorder*, Keeler was a popular staff member. Apart from his activities in connection with pH, he was a leading figure in the industrial applications of electrolytic conductance. Keeler later joined the Brown Instrument Company, but was then concerned mainly with humidity measurement, furnace-gas...
Color additives are dyes, pigments, or other substances that impart color to foods, drugs, cosmetics, and certain medical devices. Colorants are similar substances that impart color to food contact materials such as packaging. The U.S. Food and Drug Administration has the responsibility for regulating color additives and colorants, and both have premarket approval requirements. Federal oversight began in the late 19th Century and continued with the 1906 Food and Drugs Act, 1938 Federal Food, Drug, and Cosmetic Act, and multiple amendments. This chapter describes the history of U.S. regulation. Dye manufacturing in the United States was hampered by a lack of industrial chemists, limited availability of intermediates derived from coal-tar, and tariff regulations that favored imports. The first efforts are attributed to European chemists who setup rudimentary facilities in the Green Point area of Brooklyn, along the Newtown Creek. In the early 1860s, Dr. August F. W. Partz, a German chemist, attempted to manufacture magenta in a small wood building on the banks of Newtown Creek. This website is also dedicated to giving chemical industry historians and the public access to the documents and photos associated with the history of the colorants industry. British Dyestuffs Corporation Water Colour by A. Knighton-Hampton, 1919 Image Copyright of ICI. Food coloring, or color additive, is any dye, pigment or substance that imparts color when it is added to food or drink. They come in many forms consisting of liquids, powders, gels, and pastes. Food coloring is used both in commercial food production and in domestic cooking. Food colorants are also used in a variety of non-food applications including cosmetics, pharmaceuticals, home craft projects, and medical devices.