HANDBOOK OF U.S. COLORANTS FOR FOODS, DRUGS, AND COSMETICS

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PREFACE

Because of their widespread use and economic importance and the frequent controversies centered around them, much has been written about the colorants used in foods, drugs, and cosmetics. Unfortunately, what has been written is widely distributed throughout the literature. What follows is an attempt to gather together as much of this information as possible. Hopefully, this collection will serve as a manual for those who manufacture colorants, regulate their use, incorporate them into their products, study their effects, or consume the myriad of articles in which they are found. No such manual exists now.

The colorants considered here are, for the most part, only those now in use in the United States. A small number of recently delisted colorants are discussed, either because they were delisted after this work was published or because it was felt that they might still exist in products on the market and could still be of some interest. A few others not used in the United States are considered in certain analytical discussions, because their similarity to U.S. colorants might make the procedures adaptable to American products.

This handbook is divided into three parts. *Part A* provides a general background of color additives and includes information on their history and regulation, lists of currently permitted colorants, their description, properties, areas of use, specifications, and other items of interest. *Part B* deals with colorant analysis. The treatment is extensive, because the purity requirements imposed on color additives have generated a vast number of procedures. Most are given in detail; however, a few of the less important ones are summarized in the bibliographies following the various sections. Topics covered include identification, strength, moisture, metals, insolubles, inorganic salts, and colored as well as colorless impurities. *Part C,* including the resolution of mixtures and the analysis of commercial products, is somewhat of a potpourri designed to give the reader enough of a background to be able to deal with the nearly infinite number of possible situations with which he might be confronted.

Throughout this work the nomenclature is what is commonly employed in connection with color additives. Although many of the terms may appear unorthodox, they are from the jargon of the industry and will be familiar to people working in the field.

DANIEL M. MARMION

Buffalo, New York,
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CONTENTS

PART A HISTORY, REGULATION, DESCRIPTION AND USE

Chapter 1 History; Colorants in Use Today

Color is as common in our environment as the air we breathe. In fact, it is so prevalent that we are not always aware just how much we depend on it. Color is important to man as a means of identification, as a method of judging quality, and for its basic esthetic value. Consequently, it is no wonder that for centuries color has played a prominent role in three of the things most important to man—his food, medicine, and physical appearance.

History is replete with accounts of the widespread application of color additives. Paintings in Egyptian tombs dating as far back as 1500 B.C. depict the making of colored candy. Pliny the Elder tells us that wine was artifically colored four centuries before the birth of Christ, whereas the coloring of spices and condiments is known to have been practiced at least 500 years ago.

The use of colorants in drugs undoubtedly has as long a history since color has been associated with disease and its treatment since antiquity. Many such practices are documented in Egyptian papyri. The use of colorants in cosmetics was probably more widespread and certainly better documented than their application in either foods or drugs. Archeologists have evidence that Egyptians used green ore of copper as an eye shadow as early as 5000 B.C. Egyptian women are also known to have used henna to dye their hair, carmine to redden their lips, and kohl, an antimony compound, to blacken eyebrows, lids, and lashes. Thousands of years ago it was common practice in India to tint faces yellow with saffron and to dye feet red with henna. In similar times Chinese women used vegetable extracts to dye their feet, cheeks, and the tips of their tongues, whereas the men and women of Asia Minor painted their faces with litmus and marshmallow. Romans used white lead and chalk on their faces and blue and gold dyes on their hair and beards.

Until the middle of the nineteenth century the colorants used in foods, drugs, and cosmetics were materials easily obtainable from natural sources, that is, animals, vegetables, and minerals. In 1856 Sir William Henry Perkin discovered the first synthetic organic dyestuff, mauve, and soon a host of new and different colorants was added to the artist's palette.

The use of some of these in foods began in Europe almost immediately and was soon extended to drugs and cosmetics. French wines, for example, were colored with fuchsine, a triphenylmethane dye, as early as 1860. The

United States first legalized the use of synthetic organic dyes in foods by an act of Congress that authorized the addition of coloring matter to butter (August 2, 1886). The second such recognition came some 10 years later when on June 6, 1896 Congress recognized coloring matter as a legitimate constituent of cheese. By 1900 Americans were eating a wide variety of artificially colored products including ketchup, jellies, cordials, butter, cheese, ice cream, candy, sausage, noodles, and wine. The use of colorants in drug and cosmetic products was also on the increase.

This proliferation in the use of color additives was soon recognized as a threat to the nation's health. Of particular concern was the fact that poisonous substances such as chrome yellow, Martius Yellow, and quicksilver vermillion were sometimes incorporated into foods and that dyes were frequently used to hide poor quality and to add weight or bulk to certain items. Of equal concern was the fact that often little or no control was exercised over the purity of the colorants used in foods, and dyes found unsatisfactory for textiles were sometimes deliberately channeled into food products. Public awareness that such materials as arsenic acid and mercury were employed in the manufacture of various colorants soon created a fear of coal-tar dyes that lingers even today. Because of increasing public concern some measures were taken by the food manufacturers to police their own industry. An example was the list published in 1899 by the National Confectioners Association of coloring matters that they considered unfit for coloring foods. However, the effect of such actions by industry was marginal, and it was soon obvious that governmental control was necessary.

The first effective step taken by the government to check such practices was when, under the Appropriations Act of 1900 for the Department of Agriculture, the Bureau of Chemistry was given funds to investigate the relationship of coloring matters to health and to establish principles that should be followed to govern their use. Results came quickly with the issuance by the Secretary of Agriculture of a series of Food Inspection Decisions (FID). One (FID 4[3c], issued August 6, 1904) declared a food as adulterated "if it be colored, powdered or polished with intent to deceive or to make the aritcle appear of better quality than it really is". Another exempted fabricated confections from this adulteration proviso, except in those cases where the candy contained a colorant that might lead the consumer to believe that a naturally colored ingredient was present when in fact is was not. This regulation made it necessary to declare on the label the presence of such substances as imitation chocolate (FID 29, issued September 27, 1905). A third decision (FID 39, issued May 1, 1906) contained the first direct statement by the department concerning a coal-tar dye considered unsafe in foods. In effect, it stopped importation of macaroni colored with Martius Yellow.

At about the same time a thorough study was undertaken by the Department of Agriculture to determine which dyes, if any, were safe for use in foods and what restrictions should be placed on their use. This task was monumental, to say the least, and eventually included a study of the chemistry and physiology of the then nearly 700 extant coal-tar dyes as well

as the laws of various countries and states regarding their use in food products. Most of this investigation was done under the guidance of Dr. Bernard C. Hesse, whose findings were reflected in the Food and Drugs Act of 1906. This act, plus FID No. 76 (July 13, 1907) put an end to the indiscriminate use of dangerous and impure coloring matters in foods. Among other things, this new legislation required that only colors of known composition, examined physiologically and showing no unfavorable results, could be used in foods. Seven dyes were subsequently listed for use, including:

Original Name	Current Name
Amaranth	–
Ponceau 3R	–
Orange I	–
Erythrosine	FD&C Red No. 3
Naphthol Yellow S	Ext. D&C Yellow No. 7
Light Green SF Yellowish	–
Indigo Disulfo Acid, Sodium Salt	FD&C Blue No. 2

The new regulations also establish a system for certification of synthetic organic food colors by the Department of Agriculture. Certification was not mandatory, but dye manufactures soon found it to their benefit to have their products certified; the first certification took place on April 1, 1908.

Because of the increased needs of industry, the next three decades witnessed a continual growth in the use and number of color additives. The list of colors certifiable for use in foods was expanded to include the following:

Original Name	Current Name	Year Added
Tartrazine	FD&C Yellow No. 5	1916
Sudan I	–	1918
Butter Yellow	–	1918
Yellow AB	–	1918
Yellow OB	–	1918
Guinea Green B	–	1922
Fast Green FCF	FD&C Green No. 3	1927
Ponceau SX	FD&C Red No. 4	1929
Sunset Yellow FCF	FD&C Yellow No. 6	1929
Brilliant Blue FCF	FD&C Blue No. 1	1929

In 1938 a new law came into being, the Federal Food, Drug, and Cosmetic Act of 1938, instituting several new and important practices. First, it clearly stated that, henceforth, the use of any uncertified coal-tar color in any food, drug, or cosmetic shipped in interstate commerce was strictly forbidden. This restriction applied regardless of the inherent toxicity of the colorant. In effect, the colorants that could be used were limited, certification became mandatory, and governmental control was extended to the coloring of drugs

and cosmetics. Next, it created three categories* of coal-tar colors:

FD&C colors—those certifiable for use in coloring foods, drugs, and cosmetics.

D&C colors—dyes and pigments considered safe in drugs and cosmetics when in contact with mucous membranes or when ingested.

Ext. D&C colors—those colorants that, because of their oral toxicity, were not certifiable for use in products intended for ingestion, but were considered safe for use in products externally applied.

Passage of the 1938 Act launched a new series of scientific investigations and public hearings regarding the safety of the colorants then on the market. These efforts culminated in the publication in September 1940 of Service and Regulatory Announcement, Food, Drug, and Cosmetics No. 3, which listed specific colorants that could be used along with specifications and regulations relating to their manufacture, labeling, certification, and sale.

In the early 1950s, just when it appeared that the situation with regard to color additives was finally under control, new difficulties developed. The problems were precipitated by two events: a new round of pharmacological testing of food colors by the Food and Drug Administration (FDA)† and a number of cases of sickness in children who had reportedly eaten candy and popcorn colored with excessive amounts of dye. The new animal-feeding studies undertaken by the FDA were conducted at higher levels and for longer test periods than any experiments previously conducted and resulted in unfavorable findings for FD&C Orange No. 1, FD&C Orange No. 2 and FD&C Red No. 32.

The disputes that followed centered around the FDA interpretation of the 1938 act, which states that "The Secretary shall promulgate regulations providing for the listing of coal-tar colors which are harmless and suitable for use in food...." The FDA felt that "harmless" here meant that a colorant must be safe regardless of the amount used, that is, harmless per se. On the basis of this argument the FDA delisted the colorants in question. Meanwhile the food-color manufacturers argued that the FDA interpretation of the law was too strict, that a color additive need only be harmless when properly used, and that the FDA should establish safe limits. They also contended that the conditions used for the new animal feeding tests were too severe.

After a series of legal battles in the lower courts the problem was finally

*In surveying the colorants in use at the time it was discovered that several manufacturers were selling the same dyes under different names. To clearly differentiate between a textile-grade colorant and a certified colorant with the same chemical structure but having a different level of purity, and to prevent giving one manufacturer an advantage over his competitors by selecting his trade name as the official designation of a colorant to be allowed under the 1938 law, the terms FD&C, D&C, and Ext. D&C were invented.

†The FDA, which enforces the law governing color additives, was created by the Agricultural Appropriations Act of 1931.

taken to the Supreme Court, which ruled that under the 1938 law, the FDA did not have the authority to establish limits of use for colorants and that they were obligated to decertify or delist a color if any quantity of it caused harm even though lesser amounts were perfectly safe. The FDA's hands were tied. A review of the remaining colors was started, and soon several more were delisted, including FD&C Yellow Nos. 1-4. It was immediately and painfully obvious that the existing law on certifiable colors was unworkable and that the entire house of cards was about to collapse.

Through the efforts of the Certified Color Industry Committee* and the FDA a new law was formulated, the Color Additives Amendments of 1960 (Public Law 86-618). Basically, the amendments provided a much needed breathing spell. For one thing, they allowed for the continued use of existing color additives pending the completion of investigations needed to ascertain their suitability for listing as "permanent" colorants. Equally as important, they authorized the Secretary of Health, Education, and Welfare to establish limits of use, thus eliminating the controversial "harmless per se" interpretation formerly employed. Other features eliminated any distinction under the law between "coal-tar" colors and other color additives and empowered the Secretary to decide which colors must be certified and which could be exempted from certification based on their relationship to public health.

Under provisions of the new law the producers and consumers of the color additives were obliged to provide the necessary scientific data to obtain "permanent" listing of a color additive. Because of the expense involved, testing was started on only those colors that were of economic importance and, consequently, many previously certifiable colors were eventually delisted by default. The deadline or closing date for providing this data has been extended several times by the secretary, using powers granted to him by the amendments.

To date many colorants not requiring certification and a few certified colors have been "permanently" listed. The remainder of the colorants continue to be listed provisionally. Those currently in use and their status are shown in Table 1-3, and a chronological history of synthetic certifiable food colors is given in Table 4. These lists are accurate as of January 1, 1979 but are subject to change by both addition and deletion. Such changes as well as any changes in the regulations discussed in Chapter 3 are routinely published in the Federal Register.† Additional information as to what colorants can be used and the regulations pertaining to them can be obtained from the FDA, Division of Colors and Cosmetics, 200 C St., S. W. Washington, D. C. 20204.

*An informal, unincorporated association comprised of most of the food-color manufactures in the United States. The committee was formed to deal with regulatory and legislative problems affecting the entire industry and involving the FDA.

†The Federal Register is published by the office of the Federal Register, National Archives and Records Service, General Services Administration, Washington, D. C. 20408. It is distributed only through the Superintendent of Documents, U.S. Government Printing Office, Washington, D. C. 20402.

TABLE 1 COLORANTS PERMITTED IN FOODS

Food and Drug Administration Official Name	Color Index Number	Limitations[a]	Current Status
SUBJECT TO CERTIFICATION			
FD&C Blue No. 1	42090		Listed
FD&C Blue No. 2	73015		Provisional
FD&C Green No. 3	42053		Provisional
FD&C Red No. 3	45430		Listed
FD&C No. 40	16035		Listed
FD&C Yellow No. 5	19140		Listed
FD&C Yellow No. 6	15985		Provisional
Citrus Red No. 2	12156	Orange skins Only; 2.0 ppm max., based on the weight of the whole fruit	Listed
Orange B[b]	19235	Sausage and frankfurter casings or surfaces only; 150 ppm max., based on the weight of the finished product	Listed
EXEMPT FROM CERTIFICATION			
Annatto Extract	75120		Listed
β-Apo-8′-Carotenal	40820	Maximum—15 mg/lb of solid or semisolid food, or pint of liquid food	Listed
Canthaxanthin	40850	Maximum—30 mg/lb of solid or semisolid food, or pint of liquid food	Listed
Caramel			Listed
β-Carotene	75130		Listed
Carrot Oil			Listed
Cochineal Extract and Carmine	75470		Listed
Corn Endosperm Oil		Chicken feed only	Listed
Dehydrated Beets (Beet Powder)			Listed
Dried Algae Meal		Chicken feed only	Listed
Ferrous Gluconate		Ripe olives only	Listed
Fruit Juice			Listed
Grape Skin Extract		Beverages only	Listed
Paprika			Listed
Paprika Oleoresin			Listed
Riboflavin			Listed
Saffron	75100		Listed
Synthetic Iron Oxide	77491 77492 77499	Dog and cat food only; 0.25% max.	Listed
Tagetes Meal and Extract	75125	Chicken feed only	Listed
Titanium Dioxide	77891	1% Maximum in finished food	Listed

TABLE 1 Continued

Food and Drug Administration Official Name	Color Index Number	Limitations[a]	Current Status
Toasted Partially Defatted Cooked Cottonseed Flour			Listed
Turmeric	75300		Listed
Turmeric Oleoresin	75300		Listed
Ultramarine Blue	77007	Salt for animal feed only; 0.5% max.	Listed
Vegetable Juice			Listed

[a]No color additive or product containing one can be used in the area of the eye, in surgical sutures or injections unless so stated.
[b]A proposal was made in October, 1978 to delist Orange B for use in foods on the grounds that it may contain traces of 2-naphthylamine, a material considered by many to be a carcinogen. A final ruling on this proposal will probably be made while this book is in press.

TABLE 2 COLORANTS PERMITTED IN DRUGS

Food and Drug Administration Official Name	Color Index Number	Limitations[a]	Current Status
		SUBJECT TO CERTIFICATION	
FD&C Blue No. 1	42090	Ingested drugs	Listed
		Other uses	Provisional
FD&C Blue No. 2	73015	Nylon sutures only; 1% max.	Listed
		Ingested drugs	Provisional
		Other uses	Provisional
FD&C Green No. 3	42053		Provisional
FD&C Red No. 3	45430	Ingested drugs	Listed
		Other uses	Provisional
FD&C Red No. 4	14700	Externally applied drugs only	Listed
FD&C Red. No. 40	16035		Listed
FD&C Yellow No. 5	19140	Ingested Drugs	Listed
		Other uses	Provisional
FD&C Yellow No. 6	15985		Provisional
D&C Blue No. 4	42090	Externally applied drugs only	Listed
D&C Blue No. 6	73000	Sutures only; polyethylene terephthalate sutures for general surgical use, 0.2% max.; plain or chromic collagen absorbable sutures for general surgical use, 0.25% max.; plain or chromic	Listed

TABLE 2 Continued

Food and Drug Administration Official Name	Color Index Number	Limitations[a]	Current Status
		collagen absorbable sutures for opthalmic surgical use, 0.5% max.; polypropylene surgical sutures for general surgical use, 0.5% max.	
D&C Blue No. 9	69825	Cotton and silk sutures only; 2.5% max.	Listed
D&C Green No. 5	61570	Nylon 66 and Nylon 6 sutures only; 0.6% max.	Listed
		Other uses	Provisional
D&C Green No. 6	61565	Polyethylene terephthalate sutures, 0.75% max, and polyglycolic acid sutures, 0.1% max.	Listed
		Other uses	Provisional
D&C Green No. 8	59040	Externally applied drugs only; 0.01% max.	Listed
D&C Orange No. 4	15510	Externally applied drugs only	Listed
D&C Orange No. 5	45370:1	Ingested and/or internally used products, 0.75 mg max. as pure dye per daily dosage or use	Provisional
D&C Orange No. 10	45425:1		Provisional
D&C Orange No. 11	45425		Provisional
D&C Orange No. 17	12075		Provisional
D&C Red No. 6	15850		Provisional
D&C Red No. 7	15850:1		Provisional
D&C Red No. 8	15585	Ingested and/or internally used products, 0.75 mg max. as pure dye per daily dosage or use	Provisional
D&C Red No. 9	15585:1		Provisional
D&C Red No. 17	26100	Externally applied drugs only	Listed
D&C Red No. 19	45170	Ingested and/or internally used products, 0.75 mg max. as pure dye per daily dosage or use	Provisional
D&C Red No. 21	45380:2		Provisional
D&C Red No. 22	45380		Provisional
D&C Red No. 27	45410:1		Provisional
D&C Red No. 28	45410		Provisional
D&C Red No. 30	73360		Provisional
D&C Red No. 31	15800:1	Externally applied drugs only	Listed
D&C Red No. 33	17200	Ingested and/or internally used products, 0.75 mg max. as pure dye per daily dosage or use	Provisional
D&C Red No. 34	15880:1	Externally applied drugs only	Listed
D&C Red No. 36	12085	Ingested and/or internally used products, 1.7 mg max. as pure dye per daily dosage or use	Provisional