# Paper No. 13 FOOD ADDITIVES

#### Module No. 6 Colourings for the food industry - Natural colours

#### Introduction

Coloration of food, either using natural or synthetic color additives, should indicate good quality, assist marketing, and satisfy consumers. Colorants are added to food matrices in specific technological steps in order to obtain and maintain the appropriate desired colors of food products. Colorants are also used to restore natural food colors lost by exposure to air, light, temperature, moisture, or improper storage conditions.

Food colorants can also provide appropriate color to colorless foods, protect flavors and vitamins (due to their antioxidant potential) during storage, or enhance the general appeal and nutritional value of foods. Color additives are classified as dyes (pigments) or lakes. Both types can be used as primary colors (pure colors used without dilution) or secondary colors (blended primary colorants diluted with solvents or other additives). Dyes are commercial water-soluble pigments, used as powders, granules, or liquids. They are generally used in beverages, dry mixes, baked goods, confections, dairy products, etc.

Color is an important indicator of food quality. The consumer associates food color with good processing and safety.

The color of food is the result of the presence of natural pigments or of added synthetic organic dyes. Natural colorants include the pigments occurring in unprocessed food, and those that can be formed upon heating, processing, or storage.

#### Natural colours

The natural pigments may be divided into four, not necessarily homogenous, groups:

- **4** Isoprenoid derivatives carotenoids
- Forphyrins chlorophylls and hemes
- + Phenolics anthocyanins, betalains, quinones, curcuminoids
- Miscellaneous naturally occurring colorants riboflavins, caramels, melanoidins and melanins

Natural pigments are formulated either as dyes (hydrophilic powders or lipophilic oleoresins) or lakes.

#### Use of natural colours in few countries

The natural colorants included in the United States (US) category are annatto extract,  $\beta$ -apo-8'carotenal,  $\beta$ -carotene, beet powder, canthaxanthin, caramel color, carrot oil, cochineal extract (carmine), cottonseed flour (toasted, partially defatted, and cooked), ferrous gluconate, fruit juice, grape color extract, grape skin extract (enocyanin), paprika, paprika oleoresin, riboflavin, saffron, titanium dioxide, turmeric, turmeric oleoresin, vegetable juice. Examples of some exempt natural colourings include grape skin extract for restricted use only in beverages; marigold (Tagetes) meal can be used only for chicken food. The list of natural colourants with their specific properties is shown in Table 1. The properties of natural colourants is highlighted in Table 2.

Table 1. List of nationNaturalfood	EU code	Colour hue	Source and properties
colourant	Le coue	consul nuc	source una properties
Curcumin,	E 100	Orange-	Plant rhizome (Curcuma longa); strong odor
turmeric, turmeric		yellow	and bitter, sharp taste
oleoresin		J · ·	
Riboflavin (ii)	E 101	Yellow-	Semi-synthetic, obtained from bacterial
riboflavin-5-		green	fermentation (Blakeslea trispora and
phosphate		C	Ashbya gossypi); fluorescent lightsensitive,
			bitter taste
Carminic acid and	E 120	Orange to	Female cochineal insect
carmine,		red, pink to	
Cochineal extract		red	
Chlorophyll grass	E 140	Green to	Lucerne and nettle; labile to photo-oxidation
		olive	
Chlorophyllins	E 141	Bluish green	Grass, lucerne, and nettle; not claimed as
(copper complex			natural on food labels
of chlorophyll)			<b>N</b>
Caramel colours (I,	E 150a-d	Brown	Food-grade carbohydrates
II – sulfite, III –			
ammonia, IV –	ji.		
ammonia sulfite)			
Carbo medicinalis	E 153 🛛 🌔	Black	Burned plant material
(vegetable carbon)			
Carotenes	E 160a	Yellow to	Palm oil or fermentation of Blakeslea
(mixtures		orange	trispora and Ashbya gossypi; good pH
including $\beta$ -			stability, oil-soluble, easily oxidized
carotene), β-			
carotene			
Bixin, Norbixin	E 160b	Orange-red	Seeds of annatto (Bixa orellana)
Annatto extracts			
Capsanthin,	E 160c	Reddish	Paprika ( <i>Capsicum annum L.</i> )
capsorubin,		(Carmine)	
paprika, paprika		orange	
oleoresin	<b>T</b>		
Lycopene	E 160d	Orange red	Tomato ( <i>Lycopersicum esculentum</i> )
β-Apo-8-carotenal	E 160e	Orangish red	Semi-synthetic, from $\beta$ -carotene
Ethyl ester of $\beta$ -	E 160f	Orangish red	Semi-synthetic, from $\beta$ -carotene
apo-8-carotenoic			
acid			
Canthaxanthin	E 161a	Orange and	Salmon, shrimp; semi-synthetic from $\beta$ -

 Table 1. List of natural colourants with their specific properties

		pink	carotene	
Lutein	E 161b	Orange and	Aztec marigold (Tagetes sp.) petals	
		yellow		
Betanin,	E 162	Pink to red	Red beet root; heat, light and oxygen-	
Dehydrated beets			sensitive	
Anthocyanins,	E 163	Pink-red to	Elderberries, black grape skins, black	
grape color extract,		mauve-blue	carrots, red cabbages; pH-dependent, heat-	
grape skin extract			and oxidation-sensitive	
Calcium carbonate	E 170	White	Mineral rocks; surface dye	
Titanium dioxide	E 171	White	Mineral rocks; surface dye	
Iron oxides and	E 172	Yellow, red,	Mineral rocks; surface dye	
hydroxides,		black		
synthetic				
Aluminium	E 173	White	Mineral rocks; surface dye	
Silver	E 174	White	Surface dye	
Gold	E 175	Yellow	Surface dye	
Rubin BK	E 180	Red	Surface dye	
Paprika	No	Red	Paprika	
Saffron	No	Yellow-	Saffron	
		orange		

The detailed description of few natural colourants is given below.

# Caramel

Caramel color (E 150) is a dark brown or even black product used for centuries in home cooking to provide color and specific aromas to foods. Caramel shall be prepared from the food grade carbohydrates or their combinations (sucrose, glucose, fructose, invert sugar, lactose, malt syrup, molasses, starch hydrolysates and fractions there of and/or polymer thereof) in the presence of food grade acids, alkalis or salts. According to the Food and Drug Administration (FDA), caramel is the dark-brown liquid or solid material resulting from the carefully controlled heat treatment of the food-grade carbohydrates namely dextrose, invert sugar, lactose, malt syrup, molasses, starch hydrolysates and fractions thereof, sucrose.

According to FSSAI, the four types of caramel include:

**Type-I**: Plain caramel shall be prepared by heating carbohydrates with or without acids or alkalis, or their salts. Ammonium or sulphite compounds are not used.

**Type-II**: Caustic sulphite caramel shall be prepared by heating carbohydrates with or without acids or alkalis or their salt in the presence of sulphite compounds; ammonium compounds are not used.

Type - III: Ammonia process caramel shall be prepared by heating carbohydrates with or without acids or alkalis or their salts in the presence of ammonium compounds; sulphites are not used.

**Type-IV**: Ammonia sulphite caramel shall be prepared by heating carbohydrates with or without acids or alkalis or their salts in the presence of both sulphite and ammonium compounds.

Colourant	Colour	Color	Mol. Wt.	Melting	Solubility
		Index no.		point	
β-carotene	Yellow	75130	536.9	183°C	Soluble in carbon disulphide, benzene and chloroform, moderately soluble in normal hexane, cyclohexane, ether, petroleum ether and oils; practically insoluble in methanol; insoluble in water
Chlorophyll	Green	75810	893.5 (for a) 907.5 (for b)		Soluble in ethanol, ether, chloroform and benzene; insoluble in water
Caramel	Dealt separately				
Annatto	Natural orange	75120	394.5 (Bixin380.5 (Norbixin)		Norbixin is water soluble, bixin is fat soluble
Riboflavin	Yellow to Orange- yellow		376.4	280°C	Slightly soluble in water, more soluble in saline solution and in 10 % (w/v) solution of urea, sparingly soluble in alcohol, practically insoluble in chloroform and ether; but soluble in dilute solution of alkali hydroxides.

 Table 2. Properties of natural colourants used in food industry

Four classes of caramels are recognized depending on the accelerator used: burnt sugar, caustic, ammonia, and ammonium sulfite. The first is used mainly as a flavoring additive, and the other as food colorants.

Caramel colors are the most widely used food coloring agents found in a wide range of foods and beverages. Caramel represents a significant segment of the color market; about 11% of total food color production. It is obtained by heating sugars in various conditions. Caramel is the colorant soluble in water and insoluble in organic solvents.

The US Food and Drug Administration (FDA) permits the use of caramel color in food in general. Over 80% of the caramel produced in the United States is used to color soft drinks, particularly colas and root beers.

# Carotenoids

The most commonly used natural carotenoid extracts for foodstuffs are annatto, paprika, and saffron. Many other sources, including alfalfa, carrot, tomato, citrus peel, and palm oil, are also utilized. The properties of carotenoid colourants with their vitamin A activity is shown in Table 3.

**Annatto** [E 160(b)] is the orange-yellow, oil-soluble natural pigment extracted from the pericarp of the seed of the *Bixa orellana* L. tree. The major coloring component of this extract is the diapocarotenoid bixin, Several other pigments, mainly degradation products of bixin, are also present, including *trans*bixin, norbixin, and *trans*-norbixin. Bixin is a methyl ester of a dibasic fatty acid, which on treatment with alkalis is hydrolyzed to water-soluble norbixin. Two types of annatto are therefore available: the extract in oil containing bixin, and a powdered, water-soluble form containing norbixin.

Annatto butter color: Annatto extract in oil, as solution or suspension, is prepared by extraction of the outer coating of seeds with vegetable oils (singly or mixtures). The colour of annatto solution in amyl acetate at a dilution of 1:1000 (m/v), when measured in a lovibond tintometer with a 1 cm cell spectrophotometrically/calorimeterically shall be as follows: Yellow units (Min.) - 5.0; Red units (Min.) - 0.4.

Annatto cheese colour: Water soluble annatto colour is prepared by extraction of the outer coating of the seeds with aqueous alkali (NaOH or KOH – 0.5-3.0%). The colour of the solution in 0.1 N NaOH or KOH at a dilution of 1:1000 (m/v) measured in a 1-cm cell shall be: Yellow units (Min.) – 5.0; Red units (Min.) – 0.4.

**Paprika oleoresin** [E 160(c)]: is the orange-red, oil-soluble extract from sweet red peppers (*Capsicum annum*). The major coloring compounds are xanthophylls: capsanthin, capsorubin as their dilaurate esters, and  $\beta$ -carotene. The presence of characteristic flavoring and spicy pungency components limits application of this extract in foodstuffs.

Raw, unrefined palm oil contains 0.05 to 0.2% carotenoids with  $\alpha$ - and  $\beta$ -carotenes, in a ratio of 2:3, as the main constituents. It is particularly used as a colorant for margarine.

**Saffron:** It is an extract of flowers of *Crocus sativus*, contains the water-soluble pigment crocin, the digentiobioside of apocarotenic acid (crocetin), as well as zeaxanthin,  $\beta$ -carotene, and characteristic flavoring compounds. The yellow color of this pigment is attractive in beverages, cakes, and other bakery products. However, use of this colorant is restricted by its high price.

*Carrot extracts* (E 160a): Carrot extracts, carrot oil, and related plant extracts are also available in the market. Their main components are  $\beta$ - and  $\alpha$ -carotenes have been developed. Purified crystalline products contain 20%  $\alpha$ -carotene and 80%  $\beta$ -carotene. They may be used for coloring fat-based products, such as dispersion of microcrystals in oil.

Individual carotenoid compounds such as  $\beta$ -carotene,  $\beta$ -apo-8'-carotenal,  $\beta$ -apo-8'-carotenoic acid ethyl ester, and canthaxanthin are synthesized for use as food colorants for edible fats and oils. The carotenoid pigments, in combination with surface active agents, are also available as micro-emulsions for coloring foods with high water content.

Carotenoid	Color	Solubility in oil	λmax	Vitamin A
		$(g/100 \text{ cm}^3)$ at		activity (IU/mg)
		$20^{\circ}C$		
β-carotene	Yellow	0.05-0.08	455-456	1.67
β-Apo-8'-	Yellow to	0.70	448-450	1.20
carotenic	Orange			
acid ethyl ester				
β-Apo-8'-	Orange to Red	0.70-1.50	460-462	1.20
carotenal	_			
Canthaxanthin	Red	0.005	468-472	0

Table 3. Properties and vitamin A activity of carotenoid colorants

### **Turmeric and Curcumin**

Turmeric is an aromatic spice obtained from the dried ground rhizomes of *Curcuma longa* L., a perennial shrub. *Curcuma longa* L has bright green leaves, conical yellow flowers, and reaches maturity after 7 to 10 months, when rhizomes are harvested. The dried ground rhizomes yield a bright yellow powder also known as yellow ginger or Indian saffron. It has the special property of imparting both color and flavor.

The main compounds involved in color are curcumin, demethoxycurcumin, and bisdemethoxycurcumin. The three commercial forms based on *Curcuma longa* L. are turmeric powder, turmeric oleoresin, and curcumin powder. Commercially available products called curcumins contain curcumin (1,7-bis(4-hydroxy-methoxyphenyl)-1,6-heptadiene-3,5-dione) as the major component (~ 77% of total curcuminoids). Turmeric and curcumin are insoluble in water but soluble in alkalis, alcohols, and glacial acetic acid, and are used mainly as food color and secondarily as a spice. All turmeric pigments have good heat stability, but they are light sensitive.

Turmeric is used mainly as a spice, to give specific flavor and color, but also as an additive for maintaining freshness and improving the palatability and shelf lives of perishable foods. Turmeric powder is obtained from dried rhizomes. The turmeric powder standardized with maltodextrin contains 8 to 9% curcumin. The stability of turmeric under light and alkaline conditions have been increased by the addition of acids (gallic, citric, gentisic) as stabilizers. The oleoresin is obtained from turmeric powder by solvent extraction; the solvents used are ethyl acetate, acetone, carbon dioxide, dichloromethane, n-butanol, methanol, ethanol, and hexane and their mixtures; isopropanol and trichloroethylene is also one good mixture. After filtration the solvents must be completely removed from the oleoresin.

Turmeric powder and turmeric oleoresin contain pigments, flavor compounds (volatile oils), resins, and fats. Both can be used as spices and as food colorants. Curcumin powder (E 100) is obtained from the turmeric oleoresin by crystallization. It appears as an orange-yellow crystalline powder with a melting point at 179 to 182°C. It is soluble in ethanol, propylene glycol, and acetone and insoluble in water. Curcumin powder must contain minimum of 90% pigment.

Generally turmeric powder is used in mustard paste and curry powder as a colorant and for aroma. Oleoresin is added to mayonnaise, to breading of fish and potato croquettes, and to nonalcoholic beverages. However, curcumin (E 100) is added to products where turmeric is incompatible, such as cheese, butter, ice cream, and some beverages.

Other applications are coloring mustard, pickles, mayonnaise, salad dressings, oils, and cauliflower. In the European Union (EU), curcumin is permitted in alcoholic beverages (*quantum satis*), jam, jellies, marmalades (100 mg/kg), sausages, pâtés (20 mg/kg), dried potato granules and flakes, non-alcoholic drinks, and confectionery. The FDA approved turmeric powder (CI 73600) and turmeric oleoresin (CI 73615) but not curcumin powder for general use in foods. Turmeric powder is used in the 0.2 to 60 ppm range and the oleoresin in the 2 to 640 ppm range. According to Joint Expert Committee on Food Additives (JECFA), the acceptable daily intake (ADI) was established at 0 to 3 mg kg/body weight. Curcumin is a potent candidate to replace the synthetic tartrazine pigment.

# Chlorophyll

Chlorophyll, the green pigment of plants, is extracted and widely used as a colouring matter for various food items. In higher plants and algae, except the blue-greens, chlorophyll is found in chloroplasts, while in blue-green algae and photosynthetic bacteria, it is located on intracellular lamellae. In living plant tissues, in chloroplasts, chlorophyll is complexed with polypeptides, phospholipids, and tocopherols and held within hydrophobic membranes.

Typical leaf material contains about 2.5 mg/g total chlorophylls, 0.3 mg/g xanthophylls, and 0.15 mg/g carotenes. In many fruits, chlorophyll is present in the unripe state, and gradually disappears during ripening as the yellow and red carotenoids take over.

Chlorophylls are derivatives of dihydroporphirin chelated with a centrally located Mg ion. Cu or Zn ions retain the green color. The chlorophyll preparations for the food colorant market are mainly obtained from alfalfa (*Medicago sativa*) and nettles (*Urtica dioica*). Brown seaweeds are a good source of chlorophyll because as in single-cell phytoplankton, they contain chlorophyll c, which is more stable than chlorophyll a and chlorophyll b. Acetone, methanol, ethanol, and chlorinated solvents are used as extracting vehicles. The yield of extraction is ~20% in which chlorophylls, pheophytins, and other degradation products are included.

Chlorophylls are approved in Codex legislation as food additives for different applications. The oil-soluble chlorophylls, as well as the water-soluble chlorophyllins, a semi-synthetic mixture of Na and Cu salts derived from chlorophyll, have good stability in light and heat, and moderate stability with respect to both acid and alkalis. Their application as food colors is in canned products, confectionery, soups, and dairy products.

# Anthocyanins

They are present in almost all higher plants and are the dominant pigments in many fruits and flowers, giving them red, violet, or blue color. Substitution of the hydroxyl and methoxyl groups affects the color of the anthocyanins. An increase in the number of hydroxyl groups tends to

deepen the color to a more bluish shade. An increase in the number of methoxyl groups increases redness. In the presence of metals, anthocyanins can form purplish-blue or slate-gray pigments called *lakes*.

The examples of naturally occurring anthocyanidins include Pelargonidin (Orange color), cyaniding, Peonidin (orange-red color), Delphinidin, Petunidin and Malvidin (bluish-red color). The fruits potent in anthocyanins include Blackberry, Bilberry, Blackcurrant, Chokeberry, Cranberry, Strawberry and Red grapes.

Anthocyanins appear to have low stability in all products manufactured from fruits. This limits the use of these pigments as food colorants. Anthocyanin concentrate may be used as a food colorant at a pH less than 4.

### Betalains

These consist of red-violet betacyanins ( $\lambda max \sim 540$  nm) and yellow betaxanthin ( $\lambda max \sim 480$  nm). The betanin, glucoside of betanidin, is the main betalain pigment in red beetroot and accounts for 75 to 95% of total pigments in red beets. The other red pigments are isobetanin (C-15 epimer of betanin), prebetanin and isoprebetanin. The latter two are sulfate monoesters of betanin and isobetanin, respectively. The major yellow pigments are vulgaxanthin I and II. High betalain content in beetroot, on an average 1% of the total solids, makes these vegetables a valuable source of food colorants.

The color stability of betanin solution is influenced by pH and heating. Betanin is stable at pH 4 to 6, but thermostability is greatest between pH 4 and 5. Light and air have a degrading effect on betanin.

Beetroot red (E162), available as liquid beetroot concentrate and as beetroot concentrate powders, is suitable for products of relatively short shelf life, which do not undergo severe heat treatment, e.g., meat and soybean protein products, ice cream, and gelatin desserts.

Red beet betalains consisting of betanin, isobetanin, prebetanin, and smaller quantities of vulgaxanthin I and vulgaxanthin II, respectively, were proposed as viable alternatives to synthetic colorants, especially in low-acid foods such as dairy and meat products. In the latter commodities, red beet was even considered as a replacement for nitrite to achieve reddening, but it lacks the antimicrobial activity of nitrite. Moreover, red beet addition contributes to higher nitrate levels of the particular food, which represents a potential source of nitrite.

Betalains possess high molar extinction coefficients and their coloring power is comparable to that of synthetic colorants. Compared with the latter, betalains are not toxic, nor do they cause allergic reactions.

# Riboflavin

Riboflavin (E 101) is an orange-yellow crystalline powder, intensely bitter tasting, which is very slightly soluble in water and ethanol, affording a bright green-yellow fluorescent solution.

Riboflavin is stable under acid conditions, but unstable in alkaline solution and when exposed to light. Reduction produces a colorless leuco form, but color is regenerated again in contact with air.

Riboflavin-5'-phosphate sodium salt is much more soluble in water than unesterified riboflavin, and is not so intensely bitter. It is one of the physiologically active forms of vitamin  $B_2$ . It is rather more unstable to light than riboflavin. Both forms can be used as coloring and as an enriching food additive to cereal, dressing, and cheese.

# **Cochineal**, Carmine

Cochineal (E 120 – Quinone pigment) is the red coloring matter extracted from the dried bodies of female insects of the species *Dactylopius coccus* Costa or *Coccus cacti* L. These insects are cultivated on cactus plants in Peru, Equador, Guatemala and Mexico. The major pigment of cochineal is polyhydroxy anthraquinone C-glycoside, carminic acid, which may be present at up to 20% of the dry weight of the mature insects. About 80,000 to 100,000 insects provide 1 kg of raw cochineal dye. Better quality and higher commercial value of cochineal correlate with a higher ratio of red to yellow pigments.

Cochineal pigments are extracted from dried bodies of female insects with water or with ethanol; the result is a red solution that is concentrated in order to obtain the 2-5% carminic acid required for commercial cochineal. For carmine lakes, the minimum content of carminic acid is 50%.

Cochineal extract or carminic acid is rarely used as a coloring material for food, but are usually offered in the form of their lakes. Aluminum (Al) complexes (lakes) can be prepared with various ratios of cochineal and Al varying from 8:1 to 2:1, having corresponding shades from pale yellow to violet. In solution at pH 4, carminic acid is yellow to orange, depending on concentration. At alkaline pH and in the presence of metals (mainly aluminium), it becomes bluish red. Carmines are defined as the lakes of carminic acid with various metals. The most used is carmine, the aluminium lake of carminic acid.

Cochineal carmine is insoluble in cold water, dilute acids, and alcohol, and slightly soluble in alkali giving a purplish-red solution. The shade becomes bluer at higher pH. Cochineal carmine is stable in light and heat, but the stability to  $SO_2$  is poor.

In powdered form, carmine can be used for coloring various instant foodstuffs in alkaline solutions, and in ammonia for coloring different foods. Cochineal, carminic acid and carmines are approved as food colorants in the EU. The amount permitted in food ranges from 50 to 500 mg/kg. Carminic acid and carmine are considered very good food colorants due to their high stability and tinctorial properties. Solutions of carminic acid are yellow to orange, while carmines show various stable brilliant red hues. In the EU, the use of cochineal derivatives is authorized for coloring alcoholic and non-alcoholic drinks, candied fruits and vegetables, red fruit preserves, confectionery, ices, bakery products, cheeses, jam, jellies, marmalades, fruit-flavored cereals, and other products. It is currently the most robust red colorant among the authorized natural colorants, and its affinity for proteins means that it is an excellent colorant for dairy products. Cochineal added to processed pork meat provides a color similar to meat colored with erythrosine, but the color stability is higher. Cochineal can replace synthetic pigments

(tartrazine, azorubine) for coloring jellies. In the US, cochineal derivatives are permitted in amounts ranging from 0.05 to 1.0%. The JECFA considered acceptable a total ADI of 0 to 5 mg/kg of body weight for carmines as ammonium, Ca, K, or Na salts.

## Food additive regulations

The permission to use food colorants is bound to their safety and is strictly regulated by specific laws controlled at national and international levels. The natural colourants permitted by FSSAI for use in India and in US is listed in Table 4 and Table 5 respectively.

Color type	Examples
Carotene and Carotenoids	$\beta$ -carotene, $\beta$ -apo-8'- carotenal, Methyl ester of $\beta$ -apo-8'-carotenoic
	acid, Ethyl ester of $\beta$ -apo-8'-carotenoic acid, Canthaxanthin
Chlorophyll	
Riboflavin	
Caramel	
Annatto	Bixin, Norbixin
Saffron	
Curcumin or Turmeric	

### Table 4. Natural colourants permitted by FSSAI

		C	
Table 5. Application of natural colourants in food	produ	ucts as pe	r US regulations

Food product	Colourant used (allowed)	Maximum level (ppm)	
Malt bread	Caramel colours (E 150a-d)	NL	
Breakfast cereals	Carminic acid Caramel	25-200	
ALC: NOT	color-III, Carotenes, Bixin,		
	Norbixin, Capsanthin,		
	Betanin, Anthocyanins		
Chips (potato)	Curcumin, Turmeric	NL	
Butter	Carrot extract	NL	
Margarine, emulsions of fat in	Curcumin, Turmeric	10 for E 160b	
water			
Cheese	Carotenes, Bixin, Norbixin	1.5-50 for E 160b	
Vinegars and aromatic wines	Caramel colors (E 150a-d),	NL	
	Anthocyanins		
Bitter beverages	Curcumin, Turmeric, 100 mg/lit.		
	Riboflavin, Carminic acid		
Fruit and vegetable juices	Carotenes, Lycopene, β-apo-	NL	
	8-carotenal		
Beer and Cider	Caramel colors (E 150a-d)	NL	
Vegetables conserved in vinegar,	Riboflavin, Chlorophyll,	NL	
salt or oil	Caramel colors (E 150a-d),		
	Chlorophyllins, carotenes,		
	Anthocyanins		
Jams and Marmalade		5	
	Chlorophyll, Chlorophyllins,	colourants	

	Caramel colors (Ea-d),	
	Capsanthin, Paprika, Lutein,	
	Betanin, Anthocyanins,	
	Carminic acid	
Sausages, meat pastes, fish products	Curcumin, Turmeric,	20-100
	Riboflavin, Carminic acid,	
	Caramel colors (Ea-d),	
	Carotenes, Capsanthin,	
	Paprika, Betanin	
Hamburger	Carminic acid, Caramel	100 only for E 120
	colors (Ea–d)	

NL - No limit specified

#### **Preparation of colour solutions**

To prepare homogeneous solutions of water-soluble colorants, the powders or granules are dissolved in water or hydrophilic solvents (propylene glycol or glycerine), considering the solubility limits (1.5 - 4%) recommended by the manufacturer. To improve the stability of food colorants, specific permitted diluents and support matrices are used viz., lecithin, emulsifiers like polysorbates, monoglycerides and diglycerides, esters of organic acids with glycerin, esters of sucrose with fatty acids, sorbitan esters and viscosity regulating powders such as silicates.

### **Colorant stability and efficacy**

The limiting factor for the efficacy of natural colourants is stability in the watery environments found in most food matrices. Generally the factors that deteriorate colorant stability and efficacy are physical (temperature, light), chemical (oxidizing or reducing agents, acids, alkalis), and biological (enzymes, microorganisms).

# Application of natural colourants in food products

#### A. Natural colorants in beverages

Since inception, caramel colorants were used in Coca-Cola and Pepsi Cola. At present, natural colorants are becoming increasingly popular, especially in juice-containing beverages. The globalization of extraction and concentration techniques led to wider use of concentrated natural ingredients. They are easy to transport and to store and contribute to the popularity of naturally colored beverages in accordance with consumers' growing interest in quality and health protection.

Certain issues must be considered when using natural colourants in beverages. These include technical properties such as stability, sensitivity to light, pH, and temperature, and interactions with other ingredients and packaging. Some natural exempt colorants are used at concentrations of approximately 0.03 to 0.25% (annatto, cochineal, carmine, elderberry, grape skin extracts, caramel,  $\beta$ -carotene), others only as concentrates (turmeric and paprika oleoresins).

Lycopene can be used to color a variety of food products including beverages, dairy products, confectionery products, and baked goods. Tomat-O-Red (commercially produced lycopene extracted from non-GMO tomato) claims to provide health advantages (cancer preventing agent due to antioxidant potential) along with its function as a colorant.

When apples are pressed to yield juice, phloridzine, oxygen, and polyphenoloxidase enzyme combine to form phloridzine oxidation product (POP). This brilliant yellow natural colorant with nuances dependent on pH level can be incorporated easily into water-based foods such as beverages (juices, syrups) and confectionery creams, since it is stable during production processes.

### **B.** Dairy products utilizing natural colorants

Dairy product companies are now producing beverages using flavonoids and anthocyanin-rich natural juices to color milk, whey-based and fermented products. Yogurt is generally colored with hydrophilic cochineal extracts, carmine, beet juice, or FD&C Red No. 3, all of which are resistant to microbial attack. Generally, the colorant is added to the fruit preparation, but must be stabile at low pH levels. For example, beet juices are directly added to yogurt without the heat processing that may degrade the beet pigments. The most commonly used red colorants in yogurt are acid-proof cochineal extract and water-soluble carmine. Both are heat-stable at pH 2.8 to 7.0, and produce bright and appealing shades. Annatto emulsions showed less stability than annatto solutions and suspensions during continuous heating. GNT's Exberry® product, is a new fruit and vegetable extract replacing annatto which is used as additive in Cheddar and Gouda cheese production.

# C. Natural colorants in confections

Many sweets (confections) must be colored, a point in favour of their attractiveness for consumers. The commonly colored products are candies (starch jellies, candy cream centers, pan-coated candies, and hard candies), tablets, wafers, oil-based coatings, and chewing gums.

Natural colorants are rarely used for candy starch jellies due to their low stability to temperature and pH. Liquid colorants must be homogeneously incorporated into warm candy cream centers. Light discoloration is unacceptable and natural colorants are preferred. Red cochineal extracts (containing 3-4% carminic acid) are used at pH > 4 and turn orange at pH < 4, when added at the end of heat processing. Carmine lakes in alkali solutions are water soluble and may be incorporated in creams to yield bright magenta-red shades. The color can be changed by blending with yellow components ( $\beta$ -carotene or annatto). Beet juice may also provide red color but with lower heat stability and thus lower coloring power. Anthocyanins found in red cabbage, elderberry, black currant, grape juice, and grape seed concentrates are stable at pH < 3.8 and used for interior fillings but not for jellies due to their lower stability.

Orange shades are realized with lipophilic natural colorants like paprika oleoresin,  $\beta$ -carotene, and canthaxanthin after previous emulsification to yield water dispersible forms. Yellow shades can be achieved using turmeric as a water-soluble solution, but the solution is light sensitive. To maintain constant color, 3-6 ppm of  $\beta$ -carotene may be added. Stable brown coloration is

obtained from caramel; concentrated syrup is easily incorporated, well flavored and stable in creams. Colorants must be introduced into the coating syrups during production of pancoated candies. Water-soluble colorants may be used but lake pigments as dispersions are preferred. Pan-coated candies require higher concentrations of colorants than jellies or creams; they require 30 to 60 coatings of colored syrup.

Opaque coatings are obtained by combining colorants and titanium oxide, and also using FD&C lake pigments. These dispersions may also contain stabilizers, preservatives, and viscosity regulators. The critical points are temperature (< 40°C), dry matter (68 to 72%) and the ratio of tablet to coating syrup. Synthetic colorants are still preferred for coating because of better stability and lower cost, but the interest in natural colorants (turmeric, carmine, beet juice,  $\beta$ -carotene, red cabbage) in panned candies continues to increase rapidly.

Hard-boiled candies do not tolerate water after cooking, limiting the use of water-soluble colorants in vacuum cookers. The preferred method is to disperse these colorants into melted, hot candy slabs or disperse in glycerine or proplyene glycol.

Fat candies mainly need oil-based dispersion coatings but may also accept water-soluble colorants. For gum products (sticks, balls), colored lakes blended with turmeric or carmine suspended in glycerine give bright colors.

# **D.** Natural colorants in baked goods

The use of natural versus synthetic colorants and water-soluble versus oil-soluble colorants depends on the cereal or flour matrix, baking temperature regime, pH, and ability of the colorant to dissolve in the appropriate solvent. Since baked foods contain fats, the colorants must be oil-dispersible, e.g., FD&C lakes or oil-soluble natural colorants. For a good dispersion in dough, water-soluble colorants are added at 1.5-3.0% concentration. Lakes are preferred for water-based coatings due to their better light stability and non-migration from the matrix. Liquid solvents such as propylene glycol or glycerine mixed with lecithin are recommended for cookie fillings because they incorporate well into vegetable oils.

The natural colorants used often for bakery products are annatto extract or annatto plus turmeric blends (0.02-0.06 %) to obtain yellow-orange shades. Crackers are colored with annatto extract, turmeric and paprika oleoresins, or caramel. Turmeric may be used also in combination with FD&C colorants.

# Comparison of natural with synthetic permitted colourants for food

Exempt colors need to be used at higher levels than their synthetic brethren. As a consequence, they may unexpectedly change the texture, odor, or flavor of the food. They are less stable and less consistent, causing the food at times to be unacceptable to the consumer. Exempt colors are often duller, more pastel, and more easily affected by the food matrix, pH, salts, vitamins, flavors, and other factors. They are also more likely to be contaminated with undesirable trace metals, insecticides, herbicides, and bacteria.

### Epilogue

The present market for food colorants is estimated at 1 billion USD, while the natural food colorant market is only one-third of it. Synthetic colorants have achieved better results than natural or nature-identical colorants until now because of greater stability and higher ratios of coloring yield. In recent decades, the synthetic colorant market has declined, to the benefit of the natural-oriented market and consumers. In addition to the decreasing enthusiasm for chemicals in food, the high costs of toxicological studies also inhibit the development and approval of new synthetic colorants.

