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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org

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# INTRODUCTION TO THE WORLD OF NATURAL COLOUR*

Based on the work of B.S. Henry, consultant in natural food colours **

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* This document has not been edited.

** Phytone Ltd. Unit 2B Boardman Industrial Estate, Burton-on-Trent, Staffordshire, UK, DE11 9DL

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## INTRODUCTION TO THE WORLD OF NATURAL COLOUR

We live in a world of colour, colour is all about us. Colour in nature, colour in clothes and on pottery. Colour is essential to life - the colour of flowers attracts insects and chlorophyll harnesses the sun's energy.

We judge the quality of food partly by its colour - the ripeness of fruit, the freshness of vegetables. Colour is the first characteristic of food that is perceived and preconditions our expectations of the flavour of that food. Numerous trials have shown that flavour is not correctly identified when colour is not appropriate.

Food colours may be added to food for the following reasons:

(1) To compliment and enhance the flavour;

(2) To restore the original appearance of the food where colour has been destroyed by processing (e.g. canned products);

(3) To ensure uniformity of colour even though natural variations occur in the raw materials (e.g. fruit colour variation during the season;

(4) To give an attractive appearance to foods which would otherwise look unattractive (e.g. gelatin - based jelly);

(5) To assist product identification e.g. sugar confectionery which would otherwise be colourless.

A list was drawn up of those colours permitted in Europe (appendix I) and USA (app. II). These colours were then divided into the following categories:

(1) Synthetic colours - those chemically produced and which do not occur in nature;

(2) Nature identical colours - those chemically produced which are identical to those occuring in nature;

(3) Natural colours - those extracted from natural substances.

We discussed the problem of chemically modified natural extracts (e.g. sodium copper chlorophyllin and ammonium sulphite caramel) and suggested that these were synthetic colours also, though derived from a natural source.

It is important to remember that "naturalness" does not guarantee safety. Everyday foods contain toxic chemicals e.g. myristicin in carrots and nutmeg, saponins in vegetables and thioglycosides in cabbage.

JECFA (The Joint FAO/WHO Expert Committee on Food Additives) suggested that natural colours should be considered as falling within three main groups:

(1) A colour isolated in a chemically unmodified form from a recognized foodstuff and used in the foodstuff from which it is extracted at levels normally found in that food. This product could be accepted in the same manner as the food itself with no requirement for toxicological data.

(2) A colour isolated in a chemically modified form from a recognized foodstuff but used at levels in excess of those normally found in that food or used in food other than that from which it is extracted. This product might require the toxicological data usually demanded to assess the toxicity of synthetic colours.

(3) A colour isolated from a food source and chemically modified during its production or a natural colour isolated from a non-food source. These products would also require a toxicological evaluation similar to that carried out for a synthetic colour.

Since group (1) is unlikely to happen then all natural colours should be tested in a similar manner to synthetic colours.

The FDA have made a similar statement "Carotene will not be assumed to be any safer than sunset yellow nor will beet powder be considered any safer than allura red".

Thus to request the addition of a new natural colour onto the EC colour list would require considerable expense for toxicological testing (over 200,000 pounds is the likely cost). Also the petition would need to be accepted by a daunting number of committees before gaining approval. Thus the likelihood of crocin being accepted is very small.

A number of natural colours are widely used by the European Food Industry and these are listed below:

(1) Anthocyanins extracted from grape skins are manufactured in France, Italy and USA. Grapes are probably the largest crop of cultivated fruit and represent a large potential source of anthocyanins. Over 3,000 tonnes of anthocyanin extract are produced in Europe annually representing over 30 tonnes of pure pigment and about 5 million pounds in value. All this is from the by-product of wine production. The lees from grape juice production is relatively small in volume and not usually extracted for colour. The American production is considerably smaller than that of Europe.

(2) Carmine. About 60 tonnes of carmine is produced in the world each year. Most of this in Peru. Peru virtually controls this market and prices can vary significantly. A small quantity of the beetle is harvested in Europe (Canary Islands).

(3) Annatto. Another product in which Peru is dominant. Over 3,000 tonnes of seeds are harvested annually most of this from the wild. This represents about 70 tonnes of pure pigment with a value of about five million pounds.

(4) Beetroot. This is sold as a high sugar concentrate (68-70° BRIX) similar to a fruit juice concentrate. It is widely used in the dairy industry and approximately 1,000 tonnes are produced in Europe with a value of approximately two million pounds.

(5) Turmeric. This is often used in conjuction with annatto. Most turmeric is used as a ground spice in curry powders and seasonings and use as a colour is relatively small, though it is difficult to assess how much of the oleoresin is consumed as spice and how much as colour. I would estimate that 10-20 tonnes of pigment is used as colour with a value of one million pounds or thereabouts.

(6) Caramel. This is, in volume terms, the most used colour. This is not a truly natural colour. However when statisticians calculate the natural colour market caramel is usually included with the above colours.

The above values represent those of the materials as traded between colour manufacturers. The sales value to food companies is significantly more since drying, blending and packaging costs are not included. It is likely that the world natural colour market is over 100 million pounds.

## THE FUTURE

In Europe colour usage in food is decreasing slowly. However, in recent years natural colour usage has been increasing at the expense of a significant reduction in synthetic colours. It is likely that natural colour usage will not increase further in Europe and may fall slowly in volume terms and fall more quickly in relative value.

Conversely, it is possible that foodstuffs with a secondary effect will replace some colour usage as the trend to a more natural image intensifies. Additive free products are more likely to gain customer approval.

## PRODUCTION

### ANTHOCYANINS

Can in theory be extracted from a wide range of fruits and vegetables. However, grapes are by far the most important source. The juice of Vitis labrusca grapes can provide a suitable raw material. During storage of the single strength juice at chill temperatures tartrates and pigments precipitate out of solution. This can be used as a good source of colour.

More importantly the by-product of wine production - the skins, seeds and wine - is used as a source of colour. This by-product is available in large volumes and is microbiologically unstable. It has to be processed as soon as it is received from the winery and usually such factories are located very close to the winery.

The first step is to remove the seeds mechanically and then extract the colour by one of three methods:

(1) Cold, batch process. The skins are placed in large tanks (often of 50,000 litre capacity) and covered with the extraction solvent which is usually water containing sulphurous acid. The sulphurous acid acts as a preservative and also aids pigment solubility. The same skins can be extracted two or three times until they are discarded, usually in June or July. The resultant liquid is vacuum concentrated to yield a product of approximately 25° BRIX and 1% pigment. The residual SO2 acts as a preservative. Vessels should be of plastic, glass fibre or similar. This product can by spray-dried (or oven dried) to yield a powder. Malto dextrin would be used as the carrier.

(2) Hot, continuous. A belt extractor using the same extraction solvent but at 70° C or thereabouts. Very fast (4 hours or so) but tends to also extract other (undesirable) polyphenolic compounds.

The same extractor could be used for beetroot.

(3) Extraction with alcohol acidified with citric acid or HCl. Generally, a more expensive process but allows concentrated products to be more easily prepared. A rarely used process.

ANNATTO

The seeds are harvested in Peru and other South American countries, in Central Africa and Indi_. In these countries they are extracted by one or two methods.

(1) Solvent Extraction. Using acetone or a chlorinated solvent to extract cis-bixin. Cis-bixin represents 90/95% of the pigments present in annatto seed.

(2) Aqueous Extraction

(a) Cold water agitation of the whole seed will remove the pigments present from the surface of the seed. A small quantity of acid is then added to ensure no dissolved pigment is present and the whole water phase is filtered. The material is then dried to yield a powder with 20% pigment principally cix-bixin.

(b) Alternatively the same method can be used but NaOH/KOH solution is used to hydrolyse the bixin to norbixin. The extract is filtered and treated with acid to precipitate the norbixin which is collected and dried.

(3) Vegetable Oil Extraction. Direct extraction of the whole seed with hot vegetable oil yields a solution with 0.1 - 0.5% pigment suitable for use in dairy products with a high fat content. Propylene glycol can be used in place of vegetable oil but is seldom employed.

CARMINE

Cochineal is the dried insect Coccus cacti. The major country of export is Peru. The plant used is therefore similar to that used for the extraction of norbixin.

Hot water extraction yields carminic acid (this can be spray dried to form a colour concentrate), treatment with alumina and calcium ions yields carmine. Acid will precipitate the carmine out of solution which can be collected and dried and milled to a fine powder.

BEETROOT

Beetroot is extracted in a similar way to fruit juice. In fact, apple juice can be extracted on the same plant. The beetroots are harvested in the summer and stored until required for extraction. The roots are washed and trimmed then dried before being extracted in either a continuous belt diffuser or in a hydraulic fruit press. Citric acid is usually added to maintain a juice pH in the range 4-5. The single strength juice is centrifuged, pasteurised and then concentrated to a 66-70° BRIX juice concentrate. This is stored at around 3° C preferably under nitrogen. When required for despatch to a customer it is pasteurised again and packed. A powder can be prepared from the juice by spray drying with maltodextrin as the carrier.

TURMERC, BETA-CAROTENE & PAPRIKA

All these are extracted by a very similar process. The dried, milled raw material is extracted with a suitable solvent either acetone, hexane or a chlorinated hydrocarbon. The solvent is removed and the product standardized using vegetable oil. It is possible to purify curcumin by crystallisation but B-carotene (from carrot) and paprika are usually sold as the total extract. The paprika used is not hot and thus the pungent ingredient, capsaicin is not a problem.

SPRAY DRYING

Water soluble pigments such as norbixin, anthocyanin and beetroot can all bey spray dried using malto-dextrin as the carrier. Beetroot is difficult to dry because of the high sugar level in the juice. The spray dried powder is approximately 2/3rd the strength of the juice. Anthocyanins from grape skins and norbixin are easy to spray dry. The spray drying of oil soluble is obviously more complicated. Two possible routes can be taken.

(1) To form a physical emulsion of the extract in water using gum acacia is the emulsifier and carrier. This system gives a good product but requires the use of a high shear mixer and high pressure homogeniser. The resultant powder will give a cloudy solution in water.

(2) Alternatively, the extract can be mixed with a liquid emulsifier such as lecithin, polysorbate or diglyceride ester prior to mixing with an aqueous solution of carrier and spray drying.

In this case a blend of gum acacia and modified starch (such as capsul) would give a satisfactory product. In this case, a high speed homogenizer is not required and a clearer solution is obtained. However, colour strength is usually lower than with method 1 since the liquid emulsifier is also present as well as the carrier.

Alternatively, powder colours can be manufactured by dispersing the extract onto a carrier such as starch, lactose or salt. A 2-5% spread is usual. This is a simple inexpensive process but the colour strength of the final powder is rather low.

<u>OTHER PRODUCTION/EXTRACTION METHODS</u>

(i) Supercritical CO2. Technically an ideal way to extract colour. The principle problem is the capital cost of the high pressure plant.

(ii) Tissue culuture. Is possible for anthocyanins. At present only used for SHIKONIN in Japan. Production costs are relatively high.

(iii) Breed new cultivars to give high colour levels is a distinct possibility.

(iv) Enzyme treatment to increase yields and used currently in some juice production units.

(v) Membrane filtration techniques to purify and concentrate colours are used to a limited extent. More widely used for fruit juices e.g. apple.

## APPLICATION

### Factors relating to the foodstuff that influence colour choice

(1) Required colour shade;
(2) Chemical nature of the foodstuff;
(3) Processing conditions (temperature/time);
(4) pH;
(5) Packaging;
(6) Required shelf-life and storage conditions;
(7) Processing equipment (e.g. pumps & mixers);
(8) Clarify/Opacity;
(9) Physical form (liquid, paste or powder);
(10) Microbiological resistance of the foodstuff.

### Factors relating to the colour that affect colour choice

(1) Solubility in the food and in any premix;
(2) Physical nature (liquid, powder, paste, dispersion);
(3) Physical nature of pigment (dissolved or suspended);
(4) Viscosity;
(5) Pigment structure;
(6) Presence of other ingredients (e.g. preservative, emulsifiers, etc.);
(7) Microbiological quality;
(8) ph;

(9 Electrical charge (caramel colours);
(10) Legality in the countries in which the product is to be marketed;
(11) Cost.

Factors affecting colour stability

(1) ph;
(2) Oxygen;
(3) Light;
(4) SO2;
(5) Ascorbic acid level;
(6) Temperature/time;
(7) Water activity;
(8) Metal ions;
(9) Enzyme activity;
(10) Protein & polyphenol content.

It is, however, a fairly simple process to establish which are those colours most likely to be suitable for a given application. The more difficult decision is the choice of the exact application form of that colour.

YELLOW/ORANGE COLOURS

Turmeric and annatto are the two most cost effective colours. They are always cheaper in use than crocin, B-carotene and lutein. The light stability of turmeric limits its use. Crocin is more stable than turmeric and safflower is usually more stable than crocin. B-carotene is an expensive colour but its pro-vitamin A activity may be an advantage. Lutein is very non-polar and is generally used in emulsions (in the oil phase) for soft drinks or in products of high viscosity and low water content (e.g. sugar pastes).

RED COLOURS

The choice is between:

Anthocyanins - reasonably cost effective but only suitable for very acid product. pH less than 4.0;

<u>Beetroot Red</u> - again, cost effective but not heat stable and of best stability in the range pH 4-6. Thus dairy products are an ideal application.

<u>Carmine</u> - Usually used in place of beetroot red where good stability is required. Cost in use is probably 2-3 times that of beetroot.

<u>Red Sandalwood</u> - The most expensive red colour is usually used as a spice where colour is not declared e.g. fish and meat products.

Other colour shades offer little scope for choice - copper chlorophyllins for green, caramel for brown and carbon black for black.

<u>Carmine</u>

A red colour which is the aluminium lake of carminic acid extracted from the dried insect Coccus cacti. It is one of the most stable natural colours. Its prime use is in cosmetics in the USA. In the food industry it finds application in meat products, desserts (particularly those based on gelatin), flour confectionery (it is the only natural red to withstand baking) and milk shake. The only serious limitations to its use are:

(1) Its tendency to precipitate in very acid conditions usually below ph 3.5 where the viscosity is low (e.g. soft drinks).

(2) Its relatively high price and sometimes difficult availability. Its colour shade varies slightly with pH being most orange in very acid conditions and becoming progressively redder and then bluer as the pH increases. In dairy products it is usual to add annatto to give a strawberry shade.

## BLACK

Carbon black is produced as a very fine (less than 5 microns) powder. It is so fine that it is difficult to use in a food factory so application forms are produced whereby the carbon powder is suspended in a carrier such as glucose syrup or hardened fat. The level of carbon black is usually in the range 5-15%. A higher level is usually a physical impossibility due to the viscosity of the product. Carbonis perfectly stable the only possible problems are:

(1) Often the carbon settles out of suspension:
(2) Microbiological instability of the colour.

Thus its use is primarily in very viscous sugar paste and sugar confectionery products, especially those that are of a liquorice flavour.

## CARAMEL

Caramels made from sucrose and water are natural. Caramels manufactured with sulphite, ammonium sulphite or ammonia are, in my opinion, chemically modified. Natural caramel is stable to heat, light and oxygen. The only problem is that it can precipitate in very acid conditions especially in the presence of tannins.

Natural caramel can often be declared as sugar or flavour.

## BLENDING COLOURS

To obtain intermediate colour shades it is possible to mix together two or more colour extracts.

### Curcumin/Turmeric

Can be blended with most oil soluble extracts such as paprika, chlorophyll, B-carotene and annatto. It is also just possible to blend water miscible turmeric with norbixin and copper chlorophyllin.

### Crocin

Can be blended with beetroot and copper chlorophyllin and possibly with anthocyanins though any SO2 present would bleach some of the crocin.

### Annatto

Bixin can be blended with other oil soluble colour. Norbixin with turmeric and carmine but both need care to minimise the possibility of norbixin precipitation. Annatto is not compatible with beetroot or anthocyanin.

### Beetroot

Can be blended with crocin. Should not add any significant amount of extra water since yeast growth may occur.

### Anthocyanins

Generally speaking it is not recommended to mix other colours with anthocyanins. Crocin is possible.

Paprika

Will mix with oil soluble pigments. With chlorophyll brown shades are possible.

All of the afore-mentioned information relates to liquid extracts. All powders can be mixed together but remember some powders will not dissolve in acid solutions e.g. carmine and copper chlorophyllin.

## QUALITY CONTROL/SPECIFICATIONS

International specifications are compiled by three authorities.

(1) FAO/WHO have drawn up a comprehensive range of colour specifications based upon the work of the Joint Expert FAO/WHO Committee on Food Additives (JECFA). About 127 countries contribute to this work and the specifications are offered to all nations though it is up to each nation individually to decide whether to include them in their national legislation. The FAO/FAO cannot impose. JECFA though is well respected and its views are generally accepted. Each year a report is published concerning food additives. Unfortunately, the colour specifications are not published as a single document.

(2) FDA. All colours permitted by FDA have a specification. The synthetic colour specifications are very precise, the natural colour ones are more simple. Generally, they include a solvent residue level (the same as that for spice oleoresin) together with a lead (10 ppm max) and an arsenic level (usually 3 ppm max and occasionally 1 ppm as in carmine, beet powder and grape extracts). A production method is also usually included.

(3) EC. The EC has a list of specifications which are more involved than those of the FDA and are often based on FAO/WHO specifications.

However, it should be pointed out that these have not been accepted as law. Broadly, they are observed by industry though, as discussed, some aspects of particular specifications appear incorrect (e.g. the requirement for norbixin powder prepared from solvent extracted bixin to be 95% minimum in pigment content is not possible, 40% is a more realistic figure since salts from the hydrolysis are present) others seem superfluous such as the total fatty acid content of paprika extract to be not less than 75%.

The limit on lead is 10 ppm, arsenic is 3 ppm and mercury 1 ppm.

Pesticide residues apply to food in Europe but not to food additives. Though it is reasonable to expect colours extracted from foods (e.g. grapes and beetroot) to comply with the relevant food legislation, it is usual to analyse the colour from each new crop of grapes and beetroot for pesticide residues. It is likely that pesticide residues will be more tightly controlled in future.

The food colour manufacturer has not only to meet the relevant national/international specifications but also those imposed by his customer, the food company. In addition, he will include his own colour strength and shade specification which enables him to determine his yield.

The food company will impose specifications on his supplier to ensure that the colour strength and shade, microbiological quality, viscosity (solids) and other additives are correct.

Thus a specification for a food colour should include the following information:

(1) Which international specification it meets (if any);

(2) Appearance;

(3) Short description of the product - raw material used and the presence of any additives;

(4) The colour strength specification and method used. Ideally based on an E 1% 1 cm measured spectrophotometrically.

(5) An approximate pigment content calculated from the E 1% 1 cm so that the food manufacturer can calculate his dose level in ppm of pure pigment.

(6) Particle size and moisture content (if a powder). Preservation level (if present). Solids contents (if relevant).

(7) Microbiological specification;

(8) Shelf-life (in months at a specified temperature range).

Note that the microbiological specification is extremely important especially in products that undergo a mild heat process (e.g. dairy products) or those that are reconstituted by the housewife and may be abused (e.g. dry mixes).

JECFA is particularly concerned with toxicology and uses the results of animal testing to establish and ADI (acceptable daily intake). Government then judge the safety in use of an additive by the daily intake of that additive when compared to the ADI. The ADI is defined as "the daily intake of a chemical which, during an entire lifetime, appears to be without appreciable risk on the basis of all known facts at the time". The ADI can be reassessed. It is usually based on the no-effect level of the additive when fed to rats and includes a safety factor of 100.

The toxicology of natural colours is usually more difficult to establish because of the variability of natural extracts. Ideally, a food additive should be standardized for:

(1) Composition and purity of the pigments;

(2) Nature of secondary compounds;

(3) Presence of contaminants - microbiological
- pesticidal
- heavy metals;

(4) Well documented analytical procedures.

As discussed, natural colours are variable.

TOTAL QUALITY

Quality assurance should aim for complete control of the manufacturing process. All materials should be identifiable at all times. It should be possible to trace every production batch from raw material to finished product. All records of Q.C. production and goods inwards and out should be kept in writing. The laboratory should have a manual detailing all methods used and the procedures to be operated. All production processes should be clearly recorded. Everyone should play a part in quality assurance so that a consistent finished product is produced.

An international specification is drawn up for three principle reasons:

(1) To protect the health of the consumer;

(2) To protect against fraud;

(3) To help intra-community trade.

Such a specification does not ensure that the colour performs perfectly. This is the responsibility of the colour manufacturer and the food company.

Dose levels are often specified for each colour to limit the use of that colour especially if the ADI is low e.g. curcumin. Some natural colours have and ADI - not specified (e.g. beet red, anthocyanins and chlorophyll) where colour use is small in relation to consumption of that colour in the diet.

In the USA colour dose level is not usually specified and "Good Manufacturing Practice" (GMP) is presumed.

# APPENDIX I

## COLOURS PERMITTED IN EUROPE

| Synthetic | Natural | Nature Identical |
|---|---|---|
| Tartrazine | Curcumin | Riboflavin |
| Quinoline Yellow | Cochineal/Carmine | Beta-Carotene |
| Sunset Yellow | Chlorophyll | Beta-Apocarotenal (& its ethyl ester) |
| Carmoisine | Carbon Black | Canthaxanthin |
| Amaranth | Beta-Carotene | |
| Ponceau 4R | Annatto | |
| Erythrosine | Paprika | |
| Patent Blue V | Lycopene | |
| Indigo Carmine | Lutein | |
| Copper Chlorophyll | Beetroot Red | |
| Green S | Anthocyanins | |
| Caramel | | |
| Black PN | | |

Note: Inorganic pigments are not included.
Copper chlorophyll and caramel are of natural origin.

## APPENDIX II

### COLOURS PERMITTED IN USA

Synthetic (certifiable colours)

Erythrosine

Indigo Carmine

Tartrazine

Green FCF (No. 3)

Brilliant Blue FCF

Allura Red

Sunset Yellow (provisional)

### COLOURS NOT REQUIRING CERTIFICATION

| Colour Additive | Restriction |
|---|---|
| Annatto Extract | --- |
| Beta-apo-8'- carotenal | 15 mg/lb or pt |
| Beta-carotene | --- |
| Beet Powder | --- |
| Canthaxanthin | 30 mg/lb or pt, 4.4 mg/kg (chicken feed) |
| Caramel | --- |
| Carrot Oil | --- |
| Cochineal Extract (Carmine) | --- |
| Cottonseed Flour, toasted partially defatted, cooked | --- |
| Fruit Juice | --- |
| Grape Colour Extract | Non-beverage foods only |
| Grape Skin Extract (enocianina) | For still and carbonated drinks, beverage bases and alcoholic beverages |

| Colour Additive | Restriction |
| --- | --- |
| Paprika and Paprika Oleoresin | --- |
| Riboflavin | --- |
| Saffron | --- |
| Turmeric and Turmeric Oleoresin | --- |
| Vegetable Juice | --- |