Toxicity of dyestuffs

Textile dyes

Textile dyes form a large group of textile chemicals and comprise over 8,000 different compounds with almost 40,000 commercial names. The textile industry utilises mostly reactive dyes, which are used in dyeing cellulose fibres: cotton accounts for about 40% of world fibre production .

Reactive dyes have good technical characteristics but they have been found to cause adverse effects on workers in textile factories and on the environment
The toxicity was not caused only by textile dyes but by a large number of different textile chemicals.

Some observations about synthetic dyes

Allergic dermatoses and respiratory diseases are known to be caused by reactive dyes
Contact dermatitis and asthma were also studied by Thoren et al. Other researchers have shown textile industry workers exposed to reactive dyes to have changes in their immunoglobulin levels
Mutagenicity caused by some textile dyes. Wollin et al. showed several azo dyes to have genotoxicity

What makes dyes Unsafe?

Because clothing comes into prolonged contact with one's skin, toxic chemicals are often absorbed into the skin, especially when one's body is warm and skin pores have opened to allow perspiration. We also know that some individuals have what is known as chemical sensitivity, including when exposed to garments of many types. http://www.chemicalsensitivityfoundation.org/ Symptoms in adults for chemical sensitivity range from skin rashes, headaches, trouble concentrating, nausea, diarrhea, fatigue, muscle and joint pain, dizziness, difficulty breathing, irregular heart beat, and/or seizures. Symptoms in children include red cheeks and ears, dark circles under the eyes, hyperactivity, and behavior or learning problems. See Lotusorganics.com for more information.

Synthetic dyes

- Dyes are so problematic because the families of chemical compounds that make good dyes are also toxic to humans. Each new synthetic dye developed is a brand new compound, and because it's new, no-one knows it's risks to humans and the environment.

- Many dyes like Amaranth have entered the market, then have subsequently been discovered to be carcinogenic and withdrawn. The European Union in particular has been pro-active in banning dangerous dyes and dyes formulated from toxic chemicals.

- But it's backwards to create a dye, see if it's hazardous, then ban it if so. Especially since so many dyes are known to be dangerous and carcinogenic.

Azo dyes

The chemicals used to produce dyes today are often highly toxic, carcinogenic, or even explosive. The chemical Anililine, the basis for a popular group of dyes known as Azo dyes (specifically group III A1 and A2) which are considered deadly poisons (giving off carcinogenic amines) and dangerous to work with, also being highly flammable. In addition , other harmful chemicals used in the dying process include

1) dioxin – a carcinogen and possible hormone disrupter;

2) Toxic heavy metals such as chrome, copper, and zinc – known carcinogens; and

3) Formaldehyde, a suspected carcinogen.

Not only dyes other processing chemicals are also harmful

In addition to the dyes them selves, the garment finishes are often equally as harmful. We will save discussion on garment finishes for another post, but just briefly, they are used for creating wrinkle-free, stain resistant, flame retardant, anti-static, anti-fungal, anti-bacterial, odor-resistant, permanent-press, and non-shrink fabrics. They can also be used as softening agents, and for creating other easy-care treatments. In fact it is often the dye fixative, used to bond the dye color to the fabric, that causes the most problems. All of these can be particularly challenging for people with chemical sensitivities.

What happens to Azo dyes

The discharge of highly coloured synthetic dye effluents into inland and coastal waters is an environmental problem of growing concern. The Azo synthetic dyes are extensively used in textile, paper printing, photography, pharmaceutical, food, cosmetics and other industries Approximately, 10,000 different dyes and pigments are used industrially and over 0.7 million tons of synthetic dyes are produced worldwide.

Azo dyes consist of diazotised amine coupled to an amine or a phenol and contain one or more azo linkages

Azo dyes constitute 70% of synthetic dyes produced (ETAD, 1997) and they are second only to polymers in terms of new compounds submitted for registration in the US under the Toxic Substance Control Act.

What makes Azo dyes toxic

- Azo dyes that are toxic only after reduction and cleavage of the azo linkage to give aromatic amines, mostly via intestinal anaerobic bacteria. The aromatic amines are met-abolically oxidized to reactive electrophilic species that covalently bind DNA.

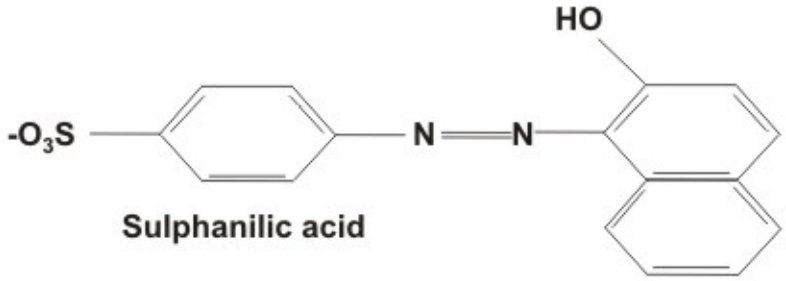
- Azo dyes with structures containing free aromatic amine groups that can be meta-bolically oxidized without azo reduction.

- Azo dyes that may be activated via direct oxidation of the azo linkage to highly reactive electrophilic diazonium salts.

Relationship of azo dye toxicity and structure

The structures of the azo dyes C.I. Food Yellow and C.I. Acid Orange 7 showing their constituent aromatic amines are illustrated in . Both compounds generate sulphanilic acid following azo bond reduction (decolourisation), but different amino-naphthols. The toxicity of Acid Orange 7 and Food Yellow were similar before reduction However, after azo bond reduction ,the toxicity of Food Yellow slightly decreased but the toxicity of Acid Orange 7 increased nearly 100-fold, Standard 1-amino-2-naphthol was very toxic compared with its sulphonated analogue (1-amino-2-naphthol-6-sulphonate. The toxicity of sulphanilic acid was equivalent to that of the unreduced dyes. Hence the increased toxicity of Acid Orange 7 after reduction was probably due to the liberation of 1-amino-2-naphthol. The toxicity of naphthol compounds varied according to the type and position of their substitution groups For example naphthalene sulphonic acid was less toxic than when the sulphonic group occurs in the 1′ position than the 2′ position respectively).

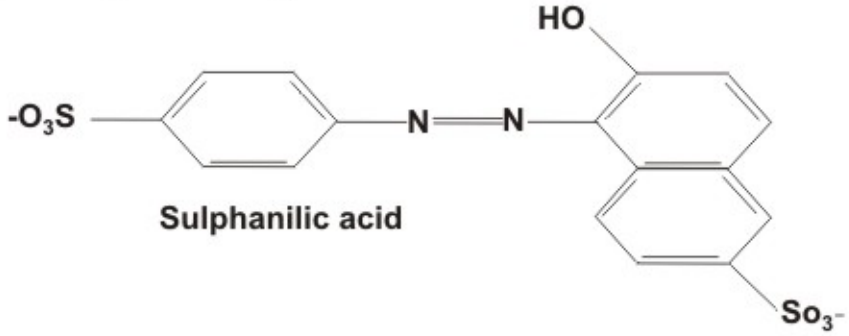
C.I. Acid orange 7



Sulphanilic acid

1-amino-2-napthol

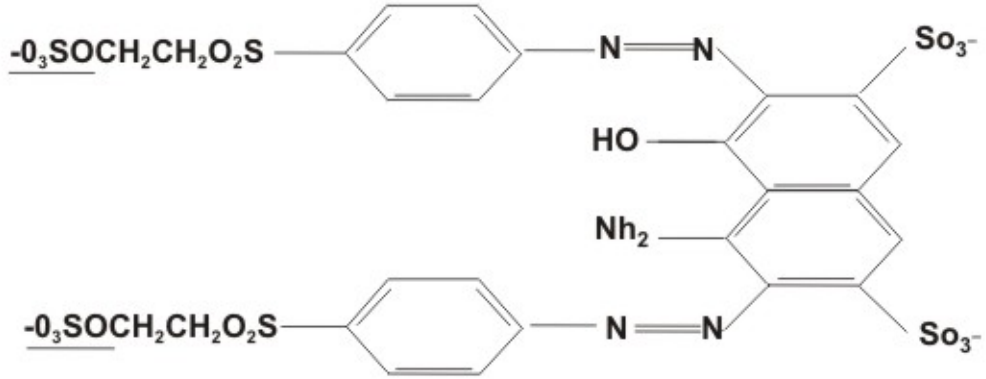
C.I. Food yellow 3(Sunset yellow FCF)



Sulphanilic acid

1-amino-2-napthol-6-sulphonate

C.I. Reactive Black 5



Diamino H-acid

Vinyl sulphone

Toxicological significance of azo dye metabolism by human intestinal microbiota

Approximately 0.7 million tons of azo dyes are synthesized each year.

Azo dyes are composed of one or more R_1-N=N-R_2 linkages. Studies have shown that both mammalian and microbial azoreductases cleave the azo bonds of the dyes to form compounds that are potentially genotoxic.

The human gastrointestinal tract harbors a diverse microbiota comprised of at least several thousand species.

Both water-soluble and water-insoluble azo dyes can be reduced by intestinal bacteria.

Azoreductases

Some of the metabolites produced by intestinal microbiota have been shown to be carcinogenic to humans although the parent azo dyes may not be classified as being carcinogenic.

Azoreductase activity is commonly found in intestinal bacteria. Three types of azoreductases have been characterized in bacteria. This review highlights how azo dyes are metabolized by intestinal bacteria, mechanisms of azo reduction, and the potential contribution in the carcinogenesis /mutagenesis of the reduction of the azo dyes by intestinal microbiota.

Acute toxicity factor

- The acute toxicity of azo dyes, as defined by the EU criteria for classification of dangerous substances, is rather low. Direct toxic levels of azo dyes will never be reached by consuming azo dye coloured food. The majority of azo dyes (food and textile) have LD50 values between 250-2,000 mg/kg body weight, indicating that for a lethal dose many grams of azo dyes have to be consumed in a singe dose. As azo dyes are highly water soluble, they do not accumulate in the body, but are metabolised in the liver and excreted in the urine. As azo dyes are very strong colour, foods normally are coloured with dyes in levels of mg dye/kg food. To reach a lethal dose an average adult person thus need to consume over 100 kg of azo coloured food in a single day.

Azo dye toxic factor

- Nevertheless some azo dyes have been banned for food use due to toxic side effects. These are not due to the dye itself, but to degradation products of the dyes.

- The azo linkage is the most labile portion of an azo dye molecule and may easily undergo enzymatic breakdown in mammals, including man. The azo linkage may be reduced and cleaved, resulting in the splitting of the molecule in two parts. This reaction is carried out by an enzyme named azo-reductase. It is a non-specific enzyme, found in various micro-organisms (such as in intestinal bacteria) and in all tested mammals.

Toxicity factors

- In mammals azo-reductases are, with different activities, present in various organs like liver, kidney, lung, heart, brain, spleen and muscle tissues. The azo-reductase of the liver, followed by the azo-reductase of the kidneys possesses the greatest enzymatic activity.

- After cleavage of the azo-linkage, the component aromatic amines are absorbed in the intestine and excreted in the urine. However, the polarity of azo dyes influences the metabolism and consequently the excretion.

- Sulphonation of azo dyes appears to decrease toxicity by enhancing urinary excretion of the dye and its metabolites. Sulphonated dyes, mainly mono-, di- and trisulphonated compounds are world-wide permitted for use in foods, cosmetics and as drugs for oral application.

- As several of the degradation products of the dyes have been found to be mutagenic or carcinogenic and subsequently, some dyes were no longer permitted as food dyes.

Food dyes

- Food dyes are one of the most widely used and dangerous additives. While the European Union has recently placed regulations on labeling food dyes to inform consumers of the health risks, the United States has no such requirement

- Here are some of the most common food dyes used today

- **Blue #1 (Brilliant Blue)**
  An unpublished study suggested the possibility that Blue 1 caused kidney tumors in mice. What it's in: Baked goods, beverages, desert powders, candies, cereal, drugs, and other products.

- **Blue #2 (Indigo Carmine)**
  Causes a statistically significant incidence of tumors, particularly brain gliomas, in male rats. What it's in: Colored beverages, candies, pet food, & other food and drugs.

- **Citrus Red #2**
  It's toxic to rodents at modest levels and caused tumors of the urinary bladder and possibly other organs. What it's in: Skins of Florida oranges.

- **Green #3 (Fast Green)**

  Caused significant increases in bladder and testes tumors in male rats. What it's in: Drugs, personal care products, cosmetic products except in eye area, candies, beverages, ice cream, sorbet; ingested drugs, lipsticks, and externally applied cosmetics.

Other food dyes

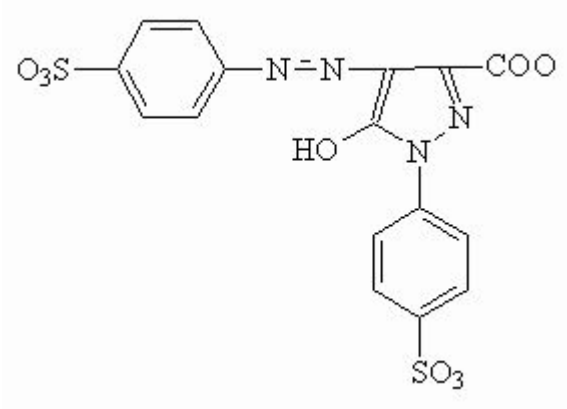
- **Red #3 (Erythrosine)**
  Recognized in 1990 by the FDA as a thyroid carcinogen in animals and is banned in cosmetics and externally applied drugs. What it's in: Sausage casings, oral medication, maraschino cherries, baked goods, candies.

- **Red #40 (Allura Red)**
  This is the most-widely used and consumed dye. It may accelerate the appearance of immune-system tumors in mice. It also causes hypersensitivity (allergy-like) reactions in some consumers and might trigger hyperactivity in children. What it's in: Beverages, bakery goods, dessert powders, candies, cereals, foods, drugs, and cosmetics.

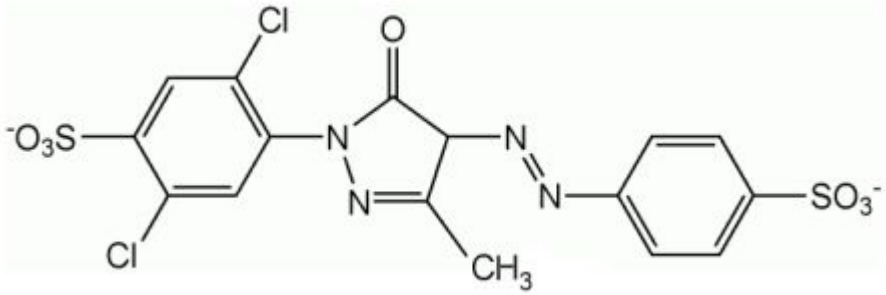
- **Yellow #5 (Tartrazine)**
  Yellow 5 causes sometimes-severe hypersensitivity reactions and might trigger hyperactivity and other behavioral effects in children. What it's in: Pet foods, numerous bakery goods, beverages, dessert powders, candies, cereals, gelatin desserts, and many other foods, as well as pharmaceuticals and cosmetics.

- **Yellow #6 (Sunset Yellow)**
  Caused adrenal tumors in animals and occasionally causes severe hypersensitivity reactions. What it's in: Color bakery goods, cereals, beverages, dessert powders, candies, gelatin deserts, sausage, cosmetics and drugs.

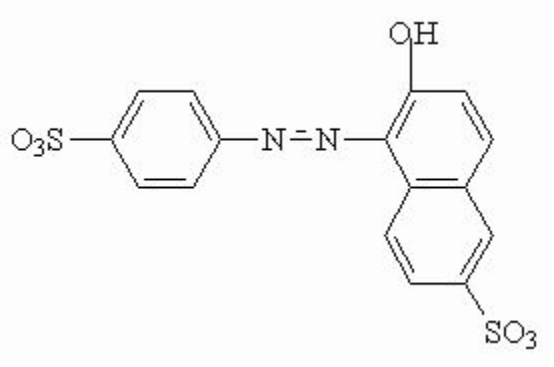
Tartrazine



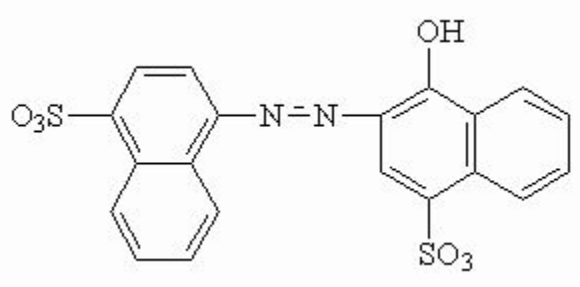
E107 : Yellow 2G



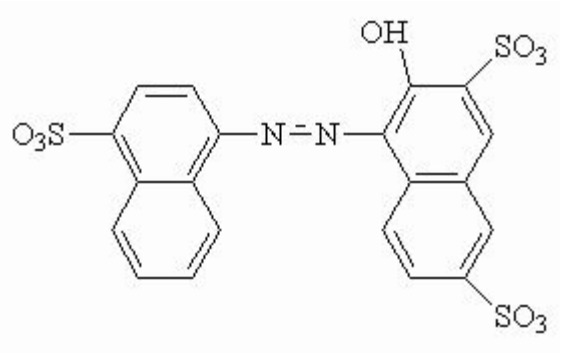
Sunset Yellow



E122 : Azorubine



E123 : Amaranth



What's the Alternative to Synthetic Dyes? Safe use of natural dyes

- So what is the dye industry doing, or rather innovators in the clothing industry who want to change the dye industry? Responsible dye manufactures are investigating ways to treat their dye effluent with organic materials and bacteria, rather than chemical treatments, and improve dye manufacture and processing to minimize hazardous chemicals used. In fact, I'm excited to learn that natural, plant based dyes are steadily making a comeback into mainstream fashion.

- While, natural dyes will never be able to completely replace synthetic dyes, due to the fact that there is only so much land to go around and food is already in great demand. However, there are innovative ways of using plants for multiple purposes and maximizing their dyeing potential. And of course, if there was a little more love for the natural colors of fabrics, dyes wouldn't be needed as much.