

CHAPTER I

INTRODUCTION

The first artificial dye, picric acid was prepared by Woulfe (1771) from the natural pigment, indigo; the second, rosolic acid, was discovered by Runge (1834). However, Perkin discovered the third artificial dye, mauvine, in 1856 and thereby founded the synthetic dye industry.

Synthetic dyes generally are aromatic organic compounds. They may be divided into three main groups :- non-ionic, anionic and cationic. The molecules of ionic (anionic or cationic) dyes are composed of two main parts, one of which is a complex aryl radical. This is the colour imparting ion. If the balance of the charge on this ion is negative then dye is classed as anionic (acidic) whereas with that being positive the dye is cationic (basic).

The second part of an ionic dye molecule is an inorganic ion (or an aliphatic organic ion or, in a few cases, an aryl ion) of charge opposite to that of the colour imparting aryl ion. The former is sometimes called the gegen ion, and the latter the dye ion. The function of the gegen ion is to balance the charge on the dye ion and to render the dye soluble in water. With a few exceptions anionic dyes are manufactured as metallic salts. The vast majority of anionic or acidic dyes are sodium salts of sulphonic acids. In the case of

cationic or basic dyes, the gegen ion is usually the chloride ion.

According to Witt (1) all coloured organic compounds contain certain groups with multiple bonds which are responsible for the colour. He termed them as chromophoric groups or chromophores e.g. nitro ($-N \begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$), nitroso ($-N=O$), azo ($-N=N-$) etc., the molecule containing the chromophoric group, a chromogen. Witt also pointed out that the presence of certain groups e.g. OH, NH₂, NHR, NR₂ etc. in the chromogen deepens colour, although these groups are not chromophores. These he called auxochromes.

Radicals which bring about deepening of colour are known as bathochromic groups, and those which bring about the opposite effect, hypsochromic groups. Deepening of colour, in colour chemistry, means the change in colour as follows : yellow → orange → red → purple → violet → blue → green → black. Since visible colour is the complementary colour of the absorbed band, bathochromic group shift the absorption maxime from the violet towards the red (i.e. they lower the frequency of the light absorbed), conversely, hypsochromic groups shift the absorption maxima from the red to the violet (i.e. they raise the frequency of the light absorbed). It has been observed that auxochromes are usually bathochromic and that replacement of hydrogen in the NH₂ group by alkyl or aryl group generally has a bathochromic effects on the other

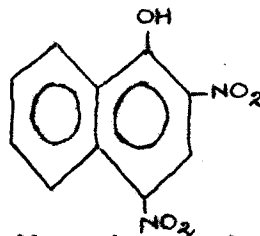
hand, acetylation of OH or NH₂ (i.e. replacement of hydrogen by an acetyl group) generally has a hypsochromic effect.

A compound containing a chromophore may be coloured, but unless an auxochrome is also present, it will not function as a dye for a textile fibre (Cf. benzene, trinitrobenzene, phenol, and picric acid).

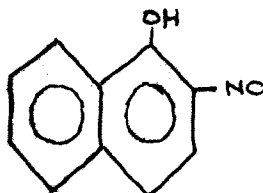
Dyes are classified according to the chemical constitution or by their application to the fibre.

Chemical classification :-

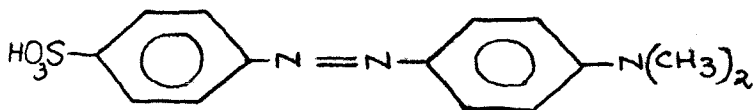
1) Nitro dyes :- These contain the nitro group as the chromophore and hydroxyl group usually as the auxochrome, e.g. Martius yellow - 2,4 dinitro-1-naphthol.



2) Nitroso dyes :- In these dyes the chromophore is the nitroso group, and the auxochrome is the hydroxyl group, e.g. Gambine R.



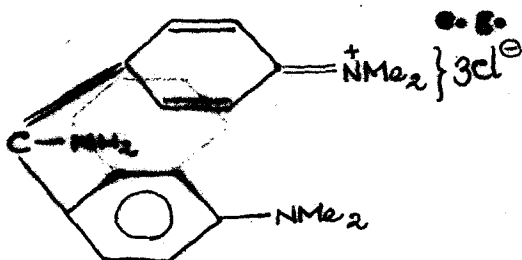
3) Azo dyes :- In azo dyes the chromophore is the azo group (N = N) and the common auxochromes are NH₂, NR₂ and OH, e.g. Methyl orange.



4) Diphenyl methane dyes :- The characteristic structural unit of these type of dyes is ---C---

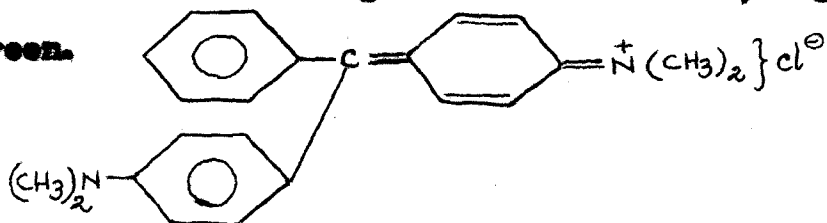


Auramine O

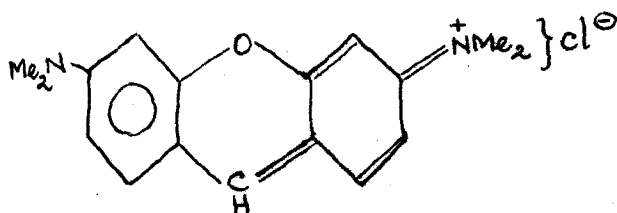


5) Triphenyl methane dyes :- This is obtained by the introduction of NH_2 , NR_2 or OH group into the rings of triphenylmethane. The products so obtained are colourless - the leuco compounds - and these, on oxidation, are converted to the corresponding tertiary alcohols - the colour bases - which readily change from the colourless benzenoid forms to the quinonoid dyes in the presence of acid owing to salt formation, e.g.

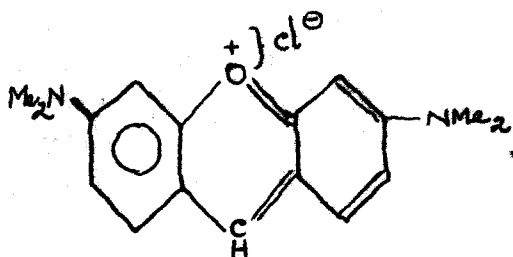
Malachite green.



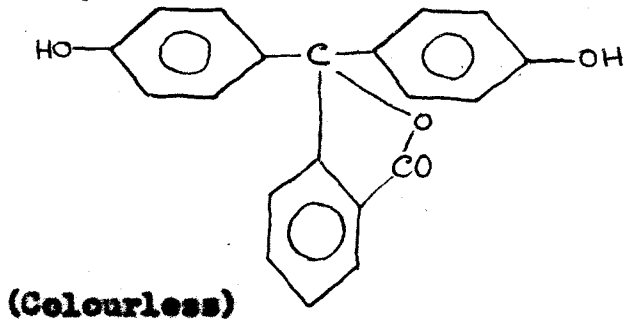
6) Xanthen dyes :- The parent substance of this group of dyes is xanthen (dibenzo-1:4-pyran), e.g. pyronines.



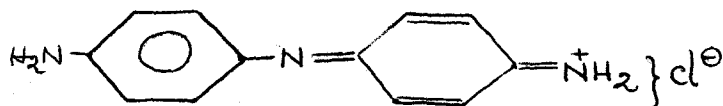
Or,



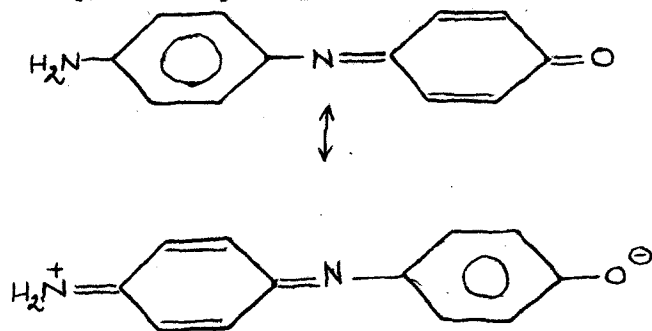
(1) Phthaleins :- A sub-group of the xanthene dyes is the phthaleins, e.g. phenolphthalein.



7) Diphenylamine (quinone-imine) dyes :- One group of these dyes is the indamines, e.g. phenylene blue.

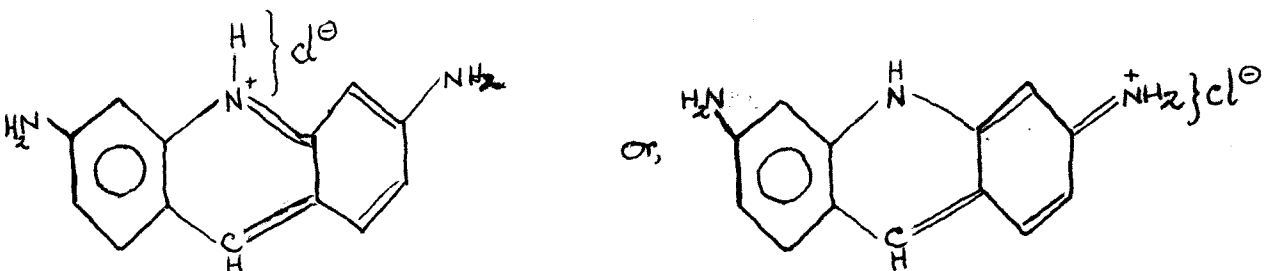


Another group is indophenols, e.g. Indophenol (blue).

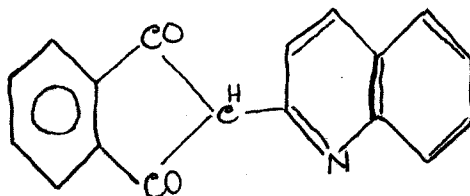


8) Heterocyclic dyes :-

(1) Acridine dye :- These are all basic dyes, e.g. 3:6 diaminoacridine,

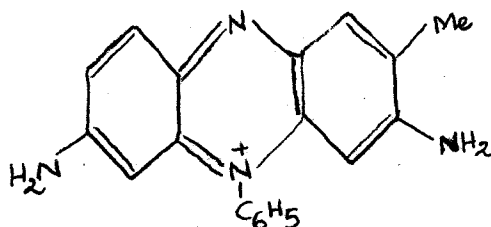


(ii) Quinoline group :- These dyes have quinoline nuclei e.g. Quinoline yellow.



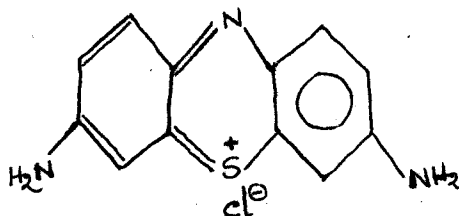
(iii) Azine dyes :-

Safranine T :-



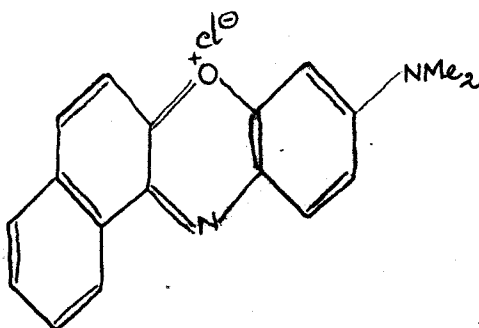
(iv) Thiazine dyes :-

Methylene Blue :-



(v) Oxazine dyes :-

Naphthol Blue :-



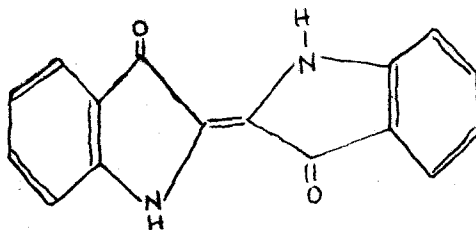
9) Vat dyes :- These are insoluble in water, but are reduced by alkaline sodium hyposulphite (dithionite) to alkali-soluble compounds which are readily reoxidised to the



dye. The characteristic structural unit of these type of dyes

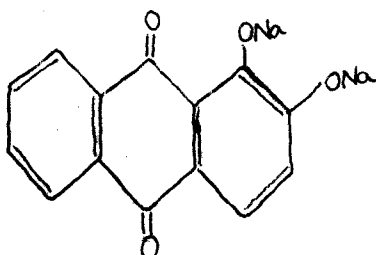


Indogotin



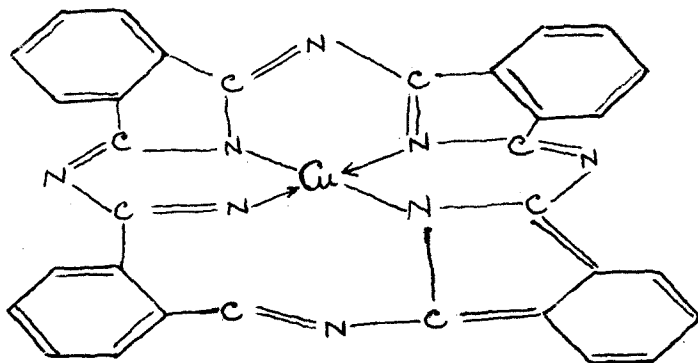
10) Anthraquinoid dyes :-

Alizarin



11) Sulphur dyes :- Sulphur dyes have complex structures, many of which are uncertain or unknown.

12) Phthalocyanine pigments and dyes :- These type of dyes contain ring systems of four isoindole units and 4-nitrogen atoms.



The primary condition for a dye — or for any chemical for that matter — to be used in feeds is that it must be nontoxic.

But the latter is a highly idealistic condition which cannot be realised in practice with an unrestricted use of chemicals in foods. The risk will always be there. Then, why use it ? For the benefit it gives. Chemicals, initially suspect, have been accepted currently for use in foods as food additives. But these have to confer the benefit of definite technological or nutritional necessity while be free from reasonable hazards to health. The latter concession has been allowed to the food additives as a compromise because absolute innocuousness is not possible. This is conceivable as these chemicals, metabolically foreign to living systems, are likely to affect, or interfere with, vital processes on the one hand and are to be metabolised and excreted, often at the expense of metabolic energy, on the other. Hence one is led to weigh benefit (of use) against risk (of the body) of the additives; when the ratio is favourable one is justified in using these.

Are the food dyes indispensable technologically ? Colouring foods artificially cannot be viewed as the same compelling need as preserving them with antimicrobials or protecting fats with antioxidants. Even if the former is granted, many opine, there are harmless natural colours like turmeric, carotenes, chlorophylls and caramel for use. But, alas, not all natural substances are harmless only because they are natural; they are also chemicals like those artificially made and have to be evaluated alike for innocuousness or otherwise. Whatever may be the controversy in this regard

chemists, food technologists and regulatory authorities of all countries have agreed to allow artificial dyes — coal-tar dyes in old terminology — in foods. Probably it is unthinkable not to have some foods in the desired colour. Tomato ketchup not in a bright hue, meat not in the expected tint and pastry without a motley of colours will not be savory items. It will also be impossible to maintain the standard appearance of a food manufactured from varying raw materials. Hence artificial dyes have been allowed in foods all over the world, but in specified items in specified concentration. The latter is intended to keep their intake below the injury level so that the use is reasonably free from hazards to health.

It will appear then that the determination of toxicity of the dyes intended for use in foods is the foremost necessity. After toxicity in different forms — chronic, acute and sub-acute, metabolic, inhalation and dermal, carcinogenicity, mutagenicity, teratogenicity, allergenicity, biochemical lesions and pathology, etc. — have been performed, the approval (of course, within the specified concentration of use) or otherwise is given.

The poisonous character of some coal-tar colours was recognized soon after their introduction in 1856. Weyl (2) and Lieber (3) pointed out some of the toxic features of coal-tar dyes. Thereafter much work has been done and is still going on regarding the toxicity of dyes for use in foods.

Metanil yellow (a widely used but nonpermitted, dye in foods in India) produces testicular degeneration in experimental animals (4, 5). Again butter yellow (6) (had earlier been in use for colouring butter), Rhodamine B (7), auramine (8), blue VRS (9) are reported to be carcinogenic. There was ulceration and abscess formation at the site of injection in rats with blue VRS (10). After the administration of congo red, lesion developed in the brain, kidney and eyes of rats (11). Malachite green increases the incidence of lung, breast, ovary and liver tumors and is known to produce inborn abnormalities of bone, skin and lung (12). Long term administration of yellow AB and yellow OB at different levels in the diet has been reported to cause varying degrees of degenerative changes in rat testis (13, 14). Moreover the dyes like auramine (15), Rhodamine B (16), malachite green (17) and Sudan III (18) which had earlier been used in foods are reported to produce pathological lesions in vital organs like kidney, spleen and liver. Again the studies on long term toxicity of some dyes, viz. chocolate brown FB (19), erythrosine (20, 21), violet 6B (22), sunset yellow (23) on various animals were proved to be nontoxic within the desired limit of use. At the same time the short term toxicity studies of violet 6B (24) and orange G (25) were also proved to be non-toxic. Also dyes to be used as food colours should preferably contain sulfonic groups in both the diazenium and coupling components. If they are made from a diazenium or a coupling component not

containing a sulfonic group one of the reduction products formed in the body will therefore be an unsulfonated aromatic amine, not readily eliminated because of its solubility in fat and this may create health hazard; some such amines are also known to be carcinogenic. Considering the toxic and non-toxic effects of different dyes some countries have permitted use of some dyes in foods. The information is given in Table 1. From Table 1 it can be observed that some dyes permitted in one country are not always permitted in another country. This is due to the fact that the dyes to be declared as permitted to be used in foods in a particular country depends upon the reasonable non-toxicity of the dye as well as upon the general health condition of the people of the country and probable estimated intake of the dyes.

Table 1

Synthetic dyes permitted in food

Commercial name	CI food number	CI constitution No.	US	EEC	UK	IN
Sunset yellow PCF	Yellow 3	15985	V	V	V	V
Tartazine	Yellow 4	19140	V	V	V	V
Amaranth	Red 9	16185	V	V	V	V
Erythrosine	Red 14	45430	V	(V)	V	V
Wool violet 5BN	Violet 2	42640	V	-	-	-

(Continued)

Table I (Contd.)

Commercial name	CI food number	CI constitution No.	US	EEC	UK	IN
Brilliant blue FCF	Blue 2	42090	V	-	-	V
Indigocarmine	Blue 1	73015	V	V	V	V
Fast green FCF	Green 3	42053	V	-	-	V
Ponceau 4R	Red 7	16255	-	V	V	V
Red FB	Red 13	14780	-	-	V	-
Fast Red B	Red 4	16045	-	-	V	V
Scarlet GN	-	14815	-	V	-	-
Ponceau 6R	Red 8	16290	-	V	-	-
Orange GGN	Orange 2	15980	-	V	-	-
Orange G	Orange 4	16230	-	-	V	-
Orange RN	Orange 1	15970	-	-	V	-
Oil yellow GG	Orange 3	11920	-	-	V	-
Yellow 2G	Yellow 5	18965	-	-	V	-
Oil yellow XP	Yellow 12	12740	-	-	V	-
Acid yellow G	Yellow 2	13015	-	V	-	-
Chrysoine S	Yellow 8	14270	-	V	-	-
Quinoline yellow	Yellow 13	47005	-	V	-	-
Green S	Green 4	44090	-	(V)	V	V
Indanthrene blue RS	Blue 4	69800	-	V	-	-

(Continued)

Table I (Contd.)

Commercial name	CI food number	CI constitution No.	US	EEC	UK	IN
Patent blue V	Blue 5	42051	-	V	-	-
Violet BNP	Violet 3	42580	-	-	V	-
Chocolate brown FB	Brown 2	-	-	-	V	-
Chocolate brown HT	Brown 3	20285	-	-	V	-
Black PN	Black 1	28440	-	V	V	-
Carmoisine	-	14720	-	-	-	V

V - Permitted ; (V) - Provisionally permitted.
 EEC - European Economic Community; US - United States.
 IN - India ; UK - United Kingdom.

Amaranth, a permitted dye in most of the country shown in Table I, has been recently banned (6) in U.S.S.R. as it has been reported to be carcinogenic in rats. This indicates that a dye proved to be non-toxic at one stage found toxic later. Hence the use of dyes in foods should preferably be minimized to technological necessity only.

Those toxicological work falling mainly within the prerogatives of biologists, one very important problem involving dyes — at least in the particular aspect — appeared to

have a potential of chemical investigation. When nitrites though hazardous could not be dispensed with for use in meat and nitrates (reducible to nitrites) occur naturally or in fertilisers, presence of nitrosamines (detected to be carcinogens) in food or their formation in vivo may be a reality. If so, what is the concentration of the components and if it constitutes any hazard with the prevailing level? The chemical reaction for the formation of nitrosamines from food dyes and their detection and estimation have been investigated from a chemical standpoint.

Toxicological green signal in favour of use of dyes presupposes control of concentration in foods. For surveillance against any health hazard and statutory or regulatory monitoring of foods in respect of the dyes used, analytical chemistry — needless to say — is of paramount importance. Qualitative analysis (detection) is necessary to check non-permitted dyes and estimation for the permissible level of concentration. Some work has been done in the field of analytical chemistry and methodology on synthetic dyes in foods.

Food~~s~~ are generally coloured with water soluble dyes and — in some cases of fatty foods, e.g. oils, butter, fats, etc. — with oil soluble colours. Natural colours in foods viz. annatto and turmeric are detected by the method of Jacobs (26), Davis (27) and Woodman (28). These methods are quite satisfactory and simple. There are a few sorting tests for oil

soluble colours. They are mainly detected by the method of Roy (29), Mitra et al. (30) and A. O. A. C. (31). But one cannot conclusively identify the particular oil soluble colour by these methods. For confirmatory detection of oil soluble colours one can adopt the methods of Janiček et al. (32) and Bose et al. (33). These two methods are simple and rapid.

There are also some preliminary sorting tests for water soluble dyes. Jacobs' wool dyeing (26) and then paper chromatography (34) is most widely accepted method for detection of water soluble colours. But one cannot detect quantitatively the colours from foods by Jacobs' method. For this alumina adsorption of Mathew et al. (35) or polyamide adsorption method of Banerjee et al. (36) are more suitable. These are general methods for detection of water soluble colours from all foods.

Some special methods for detecting water soluble colours from some particular type of foods can be mentioned here. They are methods for milk and milk products by Dhar et al. (37) and for pulses by Mitra et al. (38). By wool dyeing to some extent or by alumina adsorption one cannot easily distinguish between acid dyes and basic dyes. For separation of acid dyes and basic dyes one can adopt the electrophoresis method by Mukherjee et al. (39).

A limited attempt has been made in this investigation to make some inroads in the field, in what may be termed as analytical chemistry of food dyes. This includes a few new

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findings and confirmation of some previous knowledge particularly wherein seemed to lie gaps in our understanding of the properties and quantitation of food dyes. Some physical properties — as to how the dyes react to a few so-called physical conditions, physico-chemical properties of their absorption by fibres (advantage of utilising this property incidentally follows from selection of dyes for dyeing in preference to simply coloured compounds for tinting foods), and chemical properties — response to a few chemical reagents — have been investigated. Though the intention had originally been for applied work, very useful for judging safety of foods, reaction of some metal ions, evoked further interest in the present work for an intellectual exercise and some fundamental, physico-chemical studies have since been made.

The author is fortunate to have to work in a laboratory, and draw immensely from its analytical traditions, which has been engaged in the analytical chemistry of food dyes for more than the last twenty years and evolved, in a series of pioneering work, a large number of relevant methods. A few of such methods have been extended and some new findings, particularly the titrimetric method involving complexes soluble in water-immiscible solvents, have been recorded in the present studies.
