

400–450 nm and 580–700 nm. A qualitative inspection does not allow one to decide whether a green color originates from one dye with two absorption maxima, or from a mixture of a blue and a yellow dye.

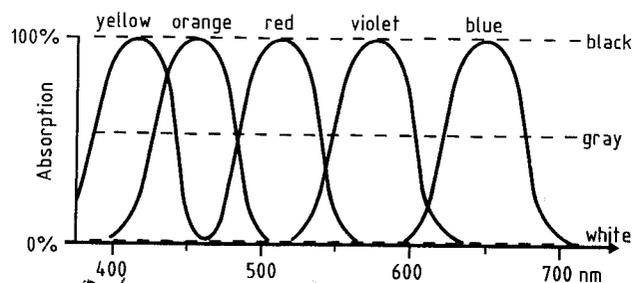


Figure 2-1. Schematic representation of the light absorption of colored solids.  
 --- achromatic colors  
 — chromatic colors

The application of two or more dyes with different absorption spectra to achieve a certain hue always leads to less brilliant shades than those obtained by applying a single dye of the required color. Such a combination is called a *subtractive mixture*. In an extreme case black is obtained since, as the sum of all dyes applied, the mixture 'subtracts' all parts of the visible spectrum.

In an analogous way, the color of a solution of colored compounds in a liquid can be explained in terms of absorbed and transmitted (rather than reflected) light.

The superposition of light from different sources may be contrasted with the subtractive process outlined above. When light from a number of sources is combined in such a way that the sum of their contributions matches the relative intensities of the visible spectrum of sunlight, an impression of colorless ('white') light is obtained. Such a combination is called an *additive mixture* of colors.

For the perception of color by the human eye, it is not only the position of the maximum of absorption with respect to wavelength (or wave number) which is important, but also the shape of the band. The smaller the width and the steeper the slopes of a band, the purer and the more brilliant the hue appears. In Figure 2-2 the spectra of two blue and one green dye are shown: Indigo is the most important dye from the point of view of the history of natural and synthetic dyes (see Sections 1.2 and 8.3). Today it is used mainly for dyeing cotton denim ('blue jeans'). Its shade is a rather dull, slightly reddish blue (so-called navy blue). The dullness is due to the broad band at 580–600 nm (half width ~ 100 nm) and the weak second band in the 400–520 nm region. Michler's Hydrol is a diphenylmethine dye (see Sec. 4.1) which is characterized by a single narrower band in the visible spectrum ( $\lambda_{\max} = 647$  nm; half width ~ 50 nm). Its color is therefore a very brilliant blue. The third spectrum is that of Malachite Green, a tri-

In contrast to indigo they are relatively narrow ( $\lambda_{\max} = 621$  and 427 nm; half widths ~ 60 and 40 nm). As mentioned above such a combination is seen by the human eye as green. The absorption of indigo is much weaker than that of the two other dyes (smaller extinction coefficient  $\epsilon$ ). This will be discussed below (Lambert-Beer law). In Section 2.7 a case is discussed in which even the slope of a band is more important for color perception than the position of its absorption maximum.

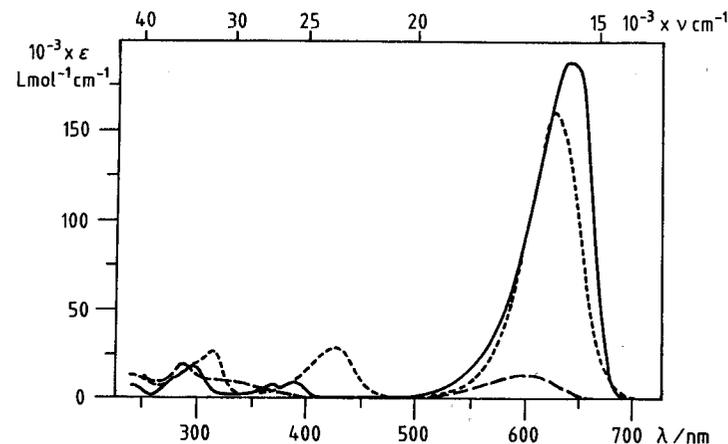


Figure 2-2. Absorption spectra of three dyes in solution (spectral data from Fabian and Hartmann, 1980).

— Indigo (in  $\text{HCl}_3$ )  
 - - - Michler's Hydrol (in water)  
 . . . Malachite Green (in water)

The industrial applicability of a colored compound depends not only on the position of the absorption band with respect to wavelength, but also the intensity of the band as a function of dye concentration. The absorption intensity may be expressed according to the Lambert-Beer law (2-1).

$$\log \frac{I_0}{I} = E = \epsilon d c \quad (2-1)$$

For technical dyes  $\epsilon$  has values ranging from  $10^4$  to more than  $10^5$   $\text{L mol}^{-1} \text{cm}^{-1}$  (see Fig. 2-2). Dyes with particularly high molar extinction coefficients (e.g. triaryl-methine dyes:  $\epsilon \geq 100\,000$ ) are efficient (in terms of color strength obtainable per mole of dye) and therefore economical. Conversely, the high prices of anthraquinone dyes are due not only to expensive intermediates, but also to their relatively low extinction coefficients.  $\epsilon$ -Values of anionic and disperse anthraquinone dyes (see Sections 8.6 and 8.7) are in the range of 8000 to 18000; vat dyes have an even lower extinction coefficient, e.g. Indanthrone (Section 8.9)  $\lambda_{\max} = 610$  nm.  $\epsilon = 2600$  in