CHAPTER 8

The Chemistry of Colour

Arguably, the seminal text on the reproduction of colour was written by R.W.G. Hunt.[1] Hunt's text covers all aspects of colour reproduction from all perspectives. The short discussion within this chapter is concerned with the chemistry of colour reproduction within the photographic system. The interested reader should consult the above reference for a more detailed account of all the many other aspects of colour science.

Dye density absorption curves for three typical dyes used in colour negative film are shown as Figure 1. In all three cases the dyes show unwanted absorptions. Dyes can be synthesised that have a much reduced half-band width. Unfortunately the use of these dyes can lead to other issues relating to the faithful reproduction of the original scene were they to be used in the construction of a film.

The curve depicted in black in Figure 1 is the integration of all three of the dye density spectra. It is not a flat line of equal dye density across all of the wavelengths, so there are colour issues that present themselves as challenges to the film builders.

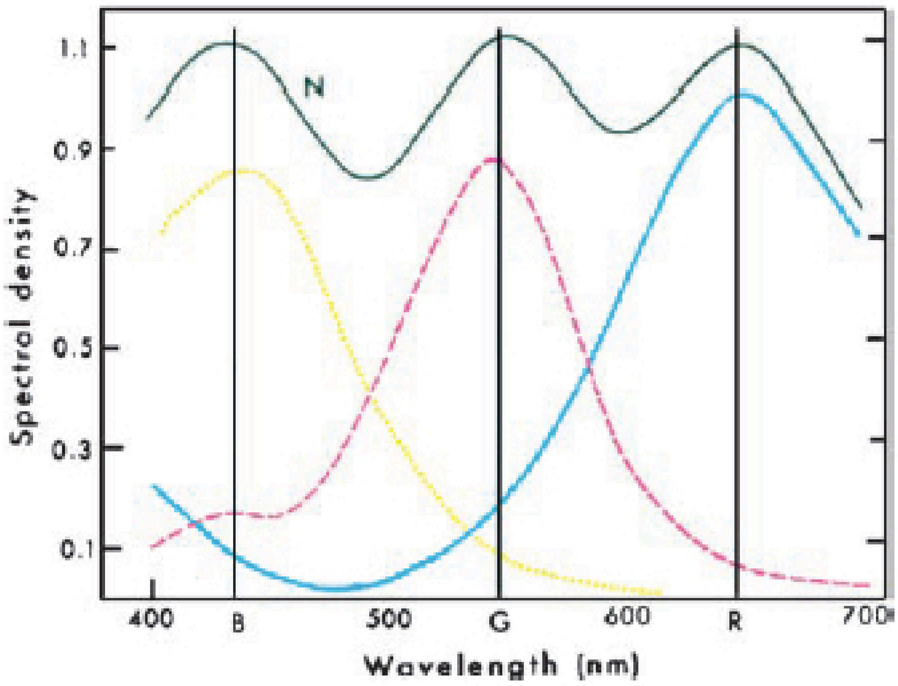

Figure 1 *Dye absorption curves for yellow, magenta and cyan dyes*

While Chapter 9 and the subsequent chapters will consider the techniques that are used to construct various films and papers, it is worthwhile showing here a curve of the photographic response of a light sensitive product to visible light. Figure 2 depicts the photographic response as measured in dye density to the logarithm of the exposure. This particular plot has been shown to be the most practical method of viewing this data and is a reproduction of Figure 17 – see Chapter 1 for more details concerning the generation of this plot.

The crucial issue is that the photographic response, *i.e.* density, to exposure produces an equal colour balance throughout the exposure range. There are several methods open to the film builder, which enable a validation that the film has faithfully recorded the colours in the original scene. The most useful chart, which is used extensively in the photographic trade, is known as the 'Macbeth checker chart' an example of which is shown as Figure 3.

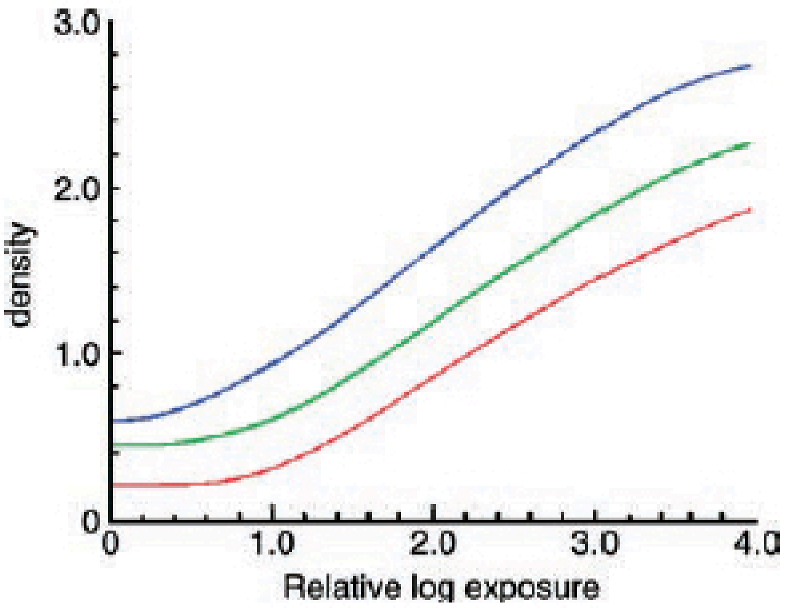

Figure 2 *Typical colour negative film density v log exposure curves*

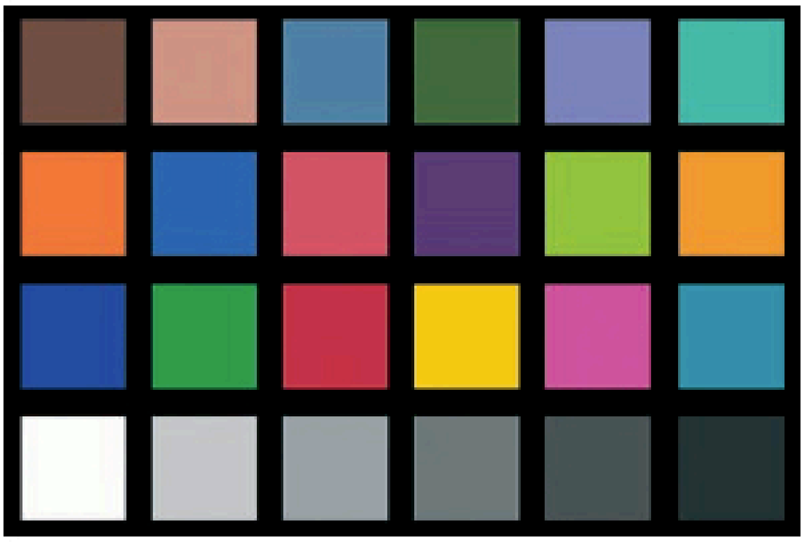

Figure 3 *A typical Macbeth colour checker chart*
(Reproduced with permission from X-rite)

Each one of the patches on the chart represents a colour that is mandated to be as accurate as possible if one is designing a film to be a faithful reproduction of an original scene. Some film manufacturers produce films which, when printed onto photographic paper, show greener greens and bluer blues. One reason for this is that holiday picture takers can look back on their holiday and be pleased that the sea was indeed blue and the grass was green – perhaps more than they realised! In practice, there is still one patch that will need to be accurately reproduced and that is on the top row second from the left – at least for white Europeans. This patch is the 'flesh' patch. No matter what the colour rendition of blues and greens, if facial colours deviate from a faithful reproduction of the original there will be problems accepting the final pictures. Flesh to neutral is always of paramount importance, especially so if the reproduced flesh patch were to have a green or blue tinge!

One of the issues faced by the technical communities of the manufacturing divisions is therefore the relative distance of one curve to each other in Figure 2. If all of the curves run 'high' or 'low' at the same time during manufacture, then the film will reproduce colours effectively (there are nevertheless limits). If on the other hand, one of the curves runs 'high' while the others are running 'low', or indeed on aim, the colour balance will be severely affected and depending on the severity it may result in the film being scrapped, Figure 4.

The same argument is valid for transparency materials and for colour paper products. Once manufactured, there is nothing that can be done to correct one colour record, without causing issues for the other colour records. This phenomenon is therefore of paramount interest to the manufacturing community during manufacture of a colour product.

Figure 1 showed the dye absorption curves of the cyan, magenta and yellow dyes produced by coupling oxidised colour developer with the

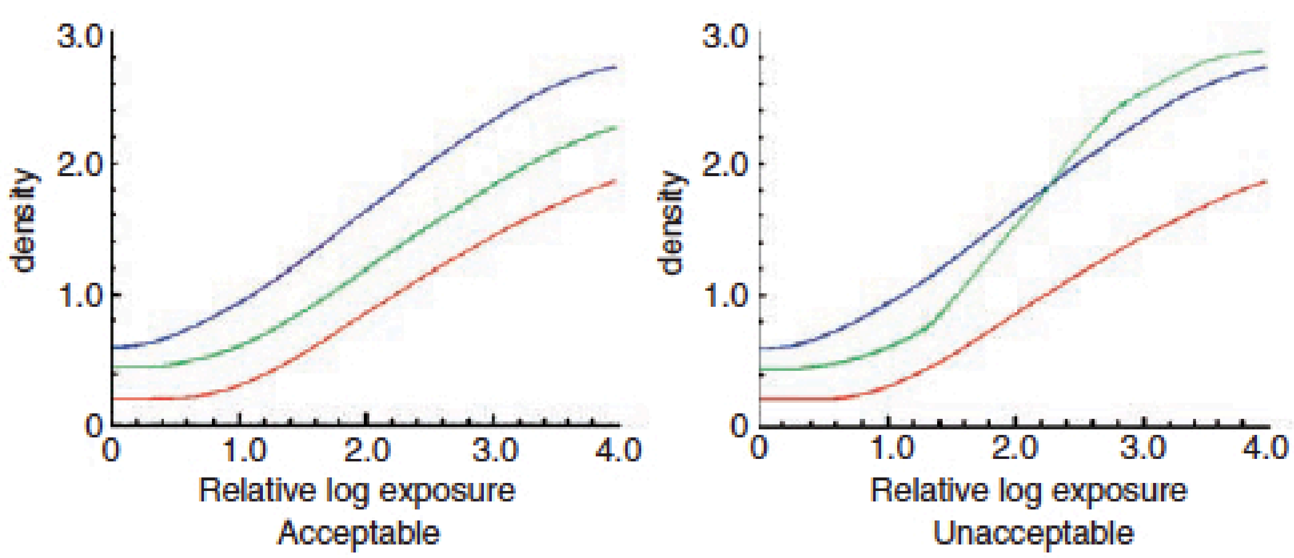

Figure 4 *Examples of acceptable and unacceptable photographic response*

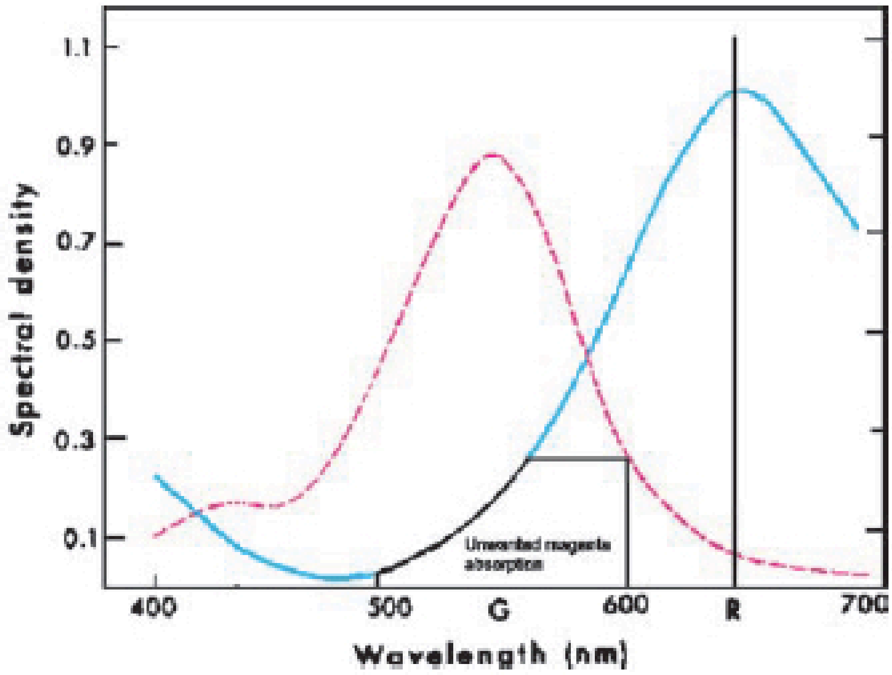

Figure 5 *Unwanted magenta dye absorption from the cyan dye*

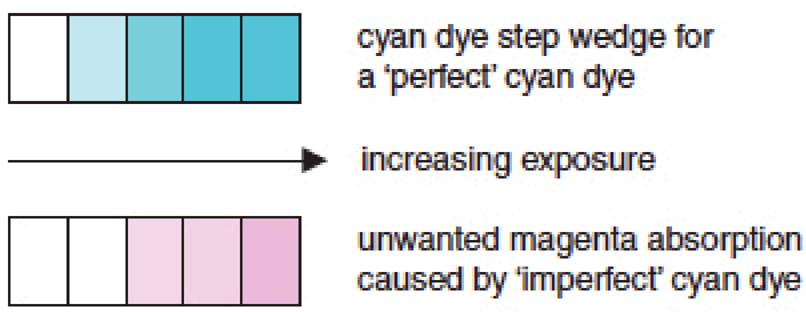

Figure 6 *Unwanted absorptions shown as a step wedge*

relevant coupler. Figure 5 shows two of these curves, namely the cyan and magenta, on the same plot.

There is a region of the absorption spectra between 500 and 600 nm where the cyan dye is contributing to the magenta absorption. There is a similar but reciprocal contribution from the magenta dye in the cyan dye region. Let us consider the consequences of one of these unwanted absorptions, and concentrate on the unwanted magenta absorption of the cyan dye. Figure 6 shows incremental steps of cyan dye, which for the purposes of this argument is assumed to be a 'pure' dye with no magenta absorptions. Underneath this step wedge is the corresponding magenta curve caused by the unwanted dye absorption from an imperfect dye.

Figures 6, 7, 8 and 9 simulate the issues concerning the unwanted absorptions using a five exposure step wedge. A test object such as this with just five steps would not be used in practice, more likely one of 21. However, this wedge adequately simulates the issues.

The magenta step wedge has been exaggerated for the purposes of argument so that the effect can be seen more clearly. In this case, the solution to the problem of cyan dye colour fidelity is to incorporate a coupler which is magenta coloured and which, when reacted with oxidised colour developer, produces a cyan dye, Figure 7.

Once again the effect has been greatly exaggerated for demonstration purposes. A conventional dispersion is made in the normal manner from these coloured couplers – see Chapter 7 for a discussion of dispersion formation. A small amount of this coupler dispersion is added to the cyan dye-forming layer, in addition to the colourless cyan dye-forming coupler previously discussed – Chapters 6 and 7. The ratio of the two couplers is of the order of 1:10 coloured to colourless coupler, but varies between the manufacturers, as the amount of unwanted dye absorption is different for the different dyes.

The combined effect of these two magenta absorptions, Figure 8, is a constant exposure of magenta dye. This additional and constant dye density can be allowed for in the printer exposure settings during the printing of the negative onto the photographic paper. Most of the manufacturers have slightly different minimum densities compared with each other, and sometimes within the films of a given film family. Printing dyes are therefore included in the film design, the amounts of which vary from film to film so that the printing density for a specific test object remains constant within a film family.

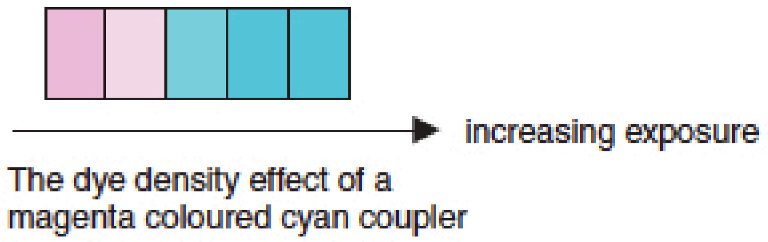

Figure 7 *A step wedge of a magenta coloured cyan coupler*

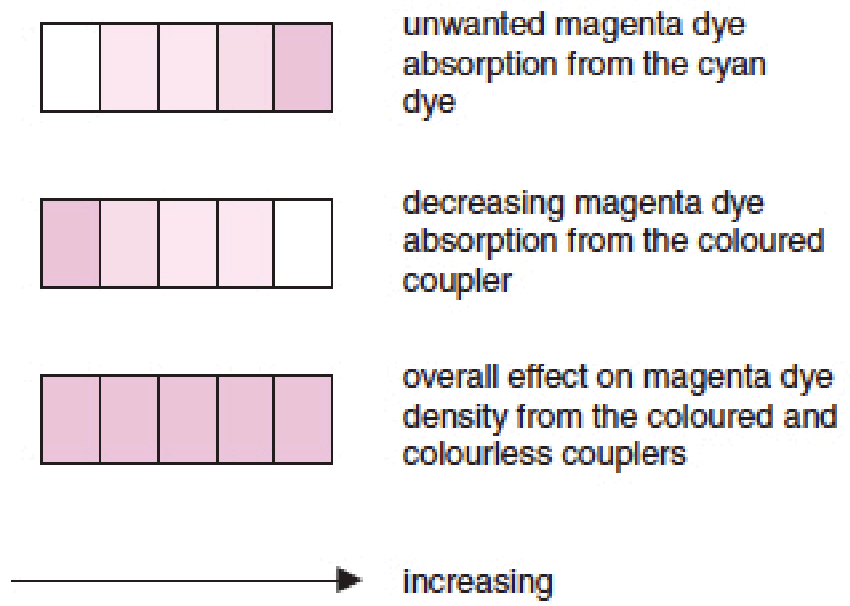

Figure 8 *Colour correction of unwanted magenta dye*

This type of colour correction is used extensively in all colour negative films, from all manufacturers. Indeed it is the effect of the coloured couplers that provide film negatives with some of their distinctive colour, often observed near the perforations, because the coloured dyes have not reacted with oxidised colour developer outside the image areas, *i.e*. near the perforations, and so the colour is a mixture of these dyes.

In practice most colour negative films only use two coloured couplers, sometimes called 'masking couplers'. The two most common masking couplers are a yellow coloured magenta dye forming coupler, and a magenta coloured cyan dye forming coupler, Figure 9.

A magenta coloured cyan coupler has the density log exposure profile of Figure 10, where red and green have been used to replace cyan and magenta, respectively, as these colours are the ones that the mask is intended to affect.

The generation of these types of masking couplers is relatively straight forward, in that it is the coupling-off group that is responsible for the initial colour. This coupling-off group has no ballast and therefore washes into the processing solutions upon processing. Care must be

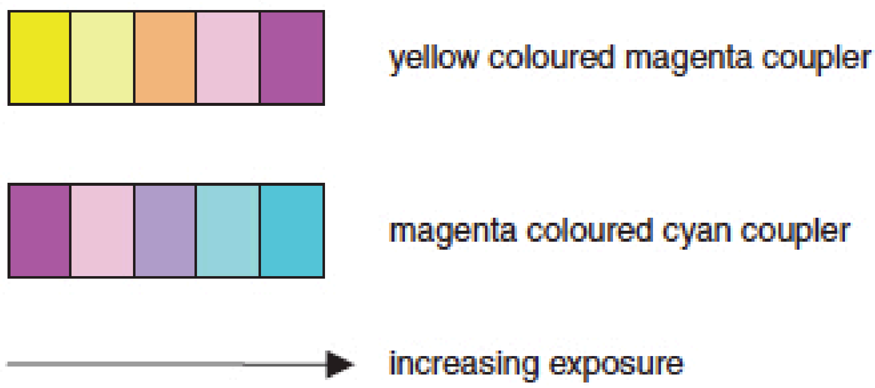

Figure 9 *Step wedges of the common colour correction couplers*

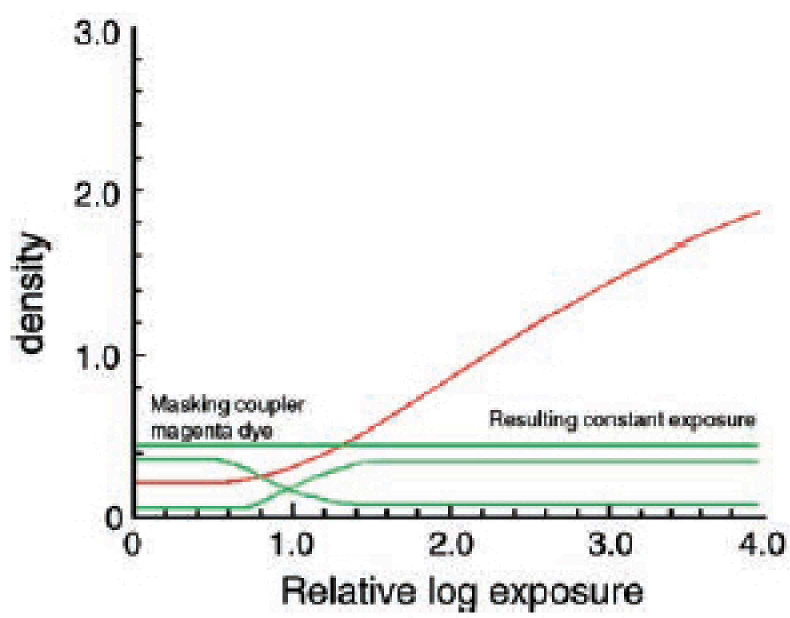

Figure 10 *Exposure curves representing colour correction*

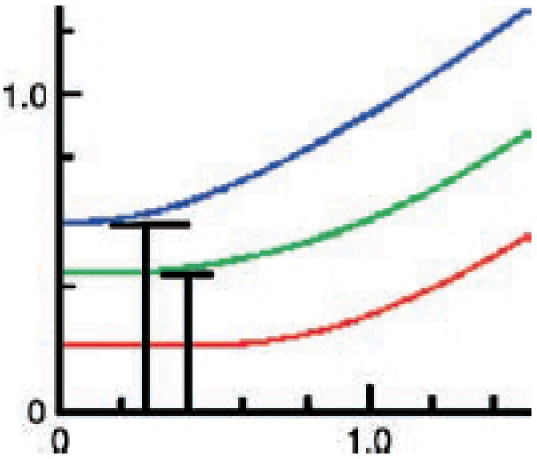

Figure 11 *The effect of printing dye density on the minimum densities of each colour record*

taken during the design of this coupling-off group that the resultant dye will not cause dye stain, when the same solutions are used to process the next film. These dyes are therefore also chosen so that they react with the sulfite or other chemicals in the processing solutions, and produce colourless bi-products.

The colours associated with processed colour negative films in the unexposed areas of the negative are therefore a mixture of the yellow and magenta dyes. As will be seen later, there is a yellow coloured layer in a colour negative film, but the colour is removed during processing and so will not be seen in the final processed film negative. These hues manifest themselves on the density/log exposure curve, Figure 2, as increased minimum density at zero exposure, Figure 11.

In this particular example of a colour negative film, the red curve has no contribution to the density from a masking coupler. Both the green and blue curves do have masking couplers coated in the relevant layers, which adds to this minimum density. Additionally, the yellow layer has a contribution from a yellow filter layer, which will be described in more detail in Chapter 9. There will be fog, or dye density, produced in non-image areas, for each of the colour records. All of the minimum densities are affected by the printing dyes mentioned above.

In general masking couplers are prepared from the reaction of the parent 2-equivalent coupler with a diazonium salt, see for example ref 2, Figure 12 or ref 3.

In this case, the coupling-off group is the 4-hydroxyphenylazo group, which will be yellow. The parent coupler is a pyrazolone, which will form a magenta dye with oxidised colour developer. The example given, Figure 12, is but one of many examples that are covered by the aforementioned patent. Clearly any aniline capable of forming a di-azonium salt can be reacted with any coupler to produce a vast range of masking couplers.