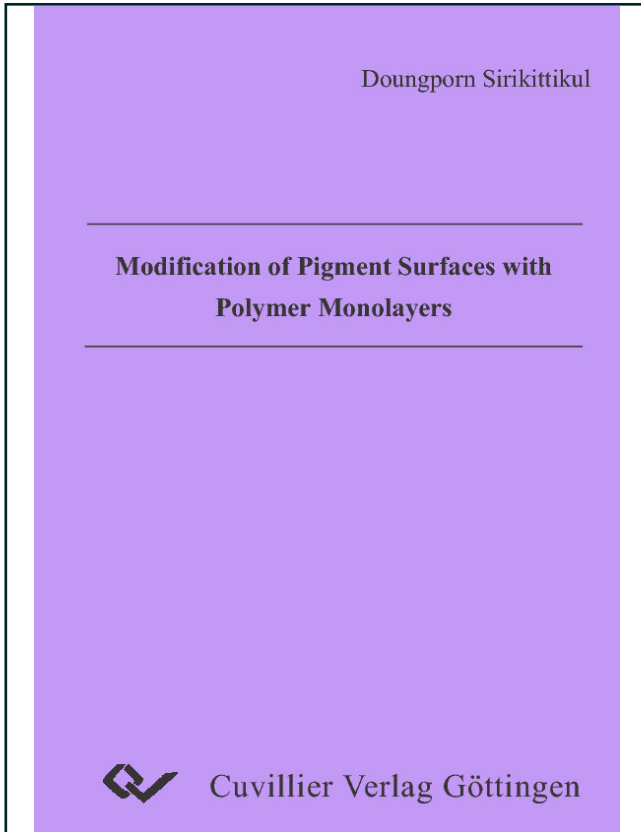




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**Modification of Pigment Surfaces with Polymer  
Monolayers**



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# 1 Introduction

## 1.1 Historical perspective

Color plays an important role in our lives. For example, in relishing food we eat or in choosing the quality of fruits or vegetables by the richness of their color. It also influences our moods and emotions. Color can be divided into *natural color*, which is around us, in the earth, sky, sea etc. and *synthetic color* which is used in textiles, paints, plastics, in a wide range of multicolored printed materials such as posters, magazines, ceramics and cosmetics. Colorant, on the other hand, can be classified into *dyes* and *pigments*<sup>1,2</sup>.

The use of color from natural resources has been known since prehistoric times (> 30 000 years ago), for example, in decorating their bodies, in coloring the furs and skins that they wore and in the painting of cave dwellings<sup>1</sup>. The dyes used to color clothing were commonly extracted either from vegetable sources including plants, trees, seeds, fruit skins etc., or from animal sources such as crushed insects and mollusks. The pigments for the paints were obtained from colored minerals such as ochre, haematite and other mineral-based pigments<sup>3</sup>.

One of the most important natural dyes, which has been used over the centuries, is indigo (s. Figure 1-1a) obtained both from dyer's woad, a plant extract in Europe, and from *Indigofera tinctoria*, a native plant of Asia. A related product is Tyrian purple (6,6'-dibromoindigo, s. Figure 1-1b), which was extracted from the glands of *Murex brandaris*, a shellfish found on the Mediterranean and Atlantic coasts<sup>2</sup>.

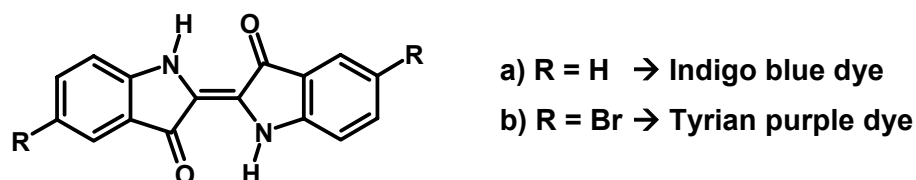


Figure 1-1: Chemical structure of a) Indigo blue and b) Tyrian purple dye.

The most important of the natural red dyes was Alizarin (1,2-dihydroxyanthraquinone; s. Figure 1-2) obtained from madder Campeachi wood extract imported from Africa<sup>1</sup>.

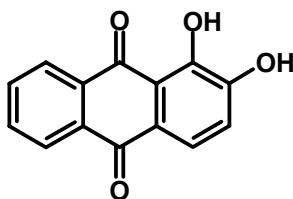


Figure 1-2: Chemical structure of 1,2-dihydroxyanthraquinone (Alizarin).

Synthetic colorants were developed by the ancient Egyptians and used in paints for many thousands of years. The earliest synthetic pigments were Alexandria blue, a ground glass colored with a copper ore, and Egyptian blue, a mixed silicate of copper and calcium, which has been identified in mural painting dating from around 1000 BC<sup>1</sup>. The oldest synthetic colorant still used today is Prussian blue (Berlin Blue), hydrated iron(III) hexacyanoferrate(II) ( $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot n\text{H}_2\text{O}$ )<sup>3</sup>.

The first synthetic dye was picric acid (s. Figure 1-3) obtained by P. Woulfe in 1771 by treating indigo with nitric acid<sup>1</sup>. A more efficient synthetic procedure to obtain picric acid using phenol as the starting material was developed many years later. This dye was used for dyeing silk giving a bright greenish-yellow. However, it did not achieve any commercial significance because of the lack of lightfastness<sup>1</sup>, i.e. low light stability.

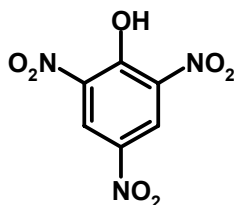


Figure 1-3: Chemical structure of picric acid.

The foundation of the synthetic dye industry is attributed to William Henry Perkin by his discovery in 1856 of a purple dye known as Mauve (s. Figure 1-4)<sup>1,2</sup>. At the beginning, the structure of Mauve was believed to be as compound a in Figure 1-4. An analytical investigation of an original sample recently showed that the dye rather is a mixture of compounds b and c. Perkin found that the crude compound produced an intense bluish purple solution with methanol and that it dyed silk in a rich color which did not wash out nor fade upon exposure to sunlight over a week. He decided to patent his discovery and to manufacture it commercially. The production started in 1857<sup>1</sup>.

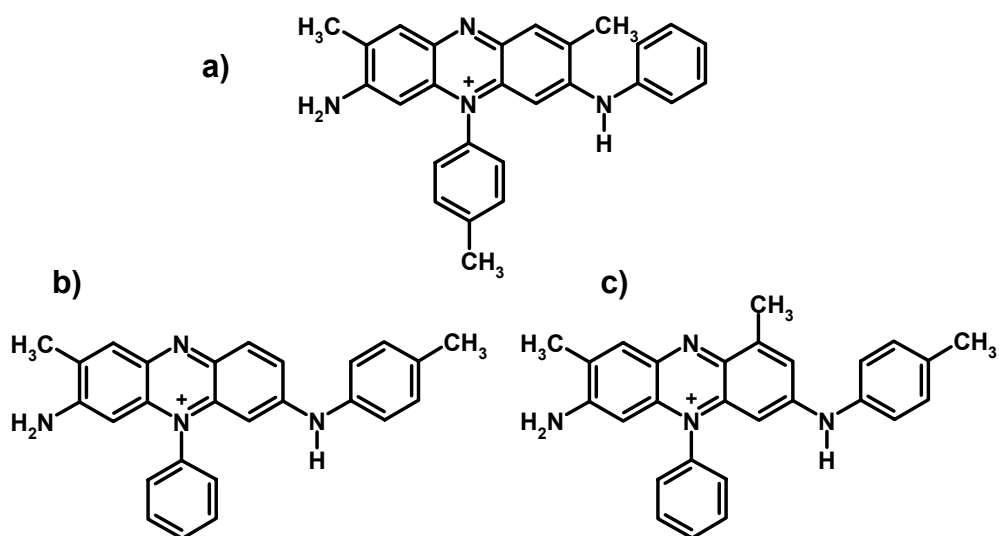


Figure 1-4: Chemical structure of Mauve dye.

In 1858, P. Griess demonstrated that the treatment of an aromatic amine with nitrous acid gave rise to an unstable salt (a diazonium salt)<sup>1</sup>. This salt could be used to prepare a colored compound. The first commercial azo dye was 4-aminoazobenzene (Aniline Yellow; s. Figure 1-5a), although it proved to have quite poor dyeing properties. A much more successful commercial product was Bismarck Brown (original named Manchester Brown; s. Figure 1-5b), which was introduced commercially in 1861<sup>1</sup>. Figure 1-5c shows the first commercial Disazo dye (Biebrich Scarlet), which was developed in 1879<sup>1</sup>.

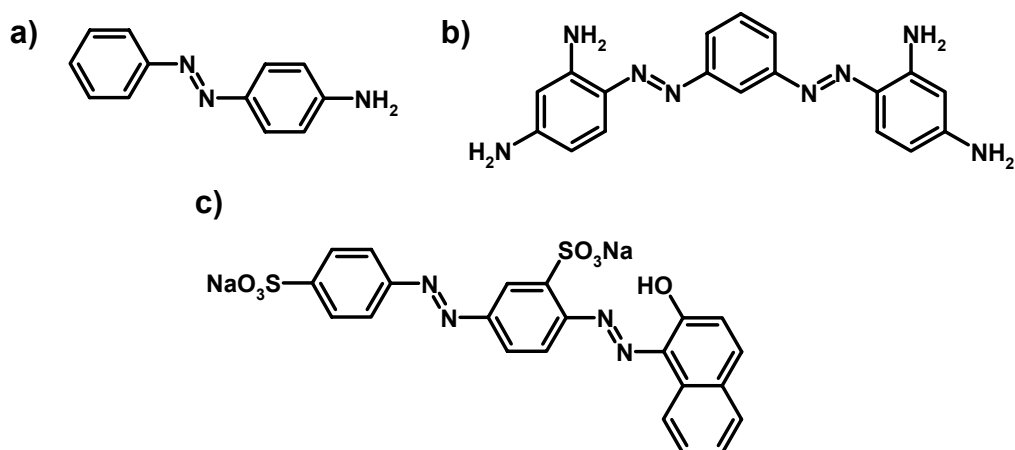


Figure 1-5: Chemical structure of azo dyes: a) Aniline Yellow, b) Bismarck Brown and c) Biebrich Scarlet.

In the late 19<sup>th</sup> century, a range of organic pigments was developed, especially for paint application. Initially, most of these pigments were obtained from water-soluble textile dyes. For example, anionic dyes were precipitated onto inert colorless inorganic substrates such as alumina and barium sulfate to give insoluble pigments. Such products were commonly referred as *lakes*<sup>1</sup>.

The first water insoluble organic pigments were the red  $\beta$ -naphthol pigments (1885), which did not contain substituents (acidic or basic groups) capable of salt formation. In 1909, Hansa Yellow (s. Figure 1-6) was introduced to the market as the first monoazo yellow pigment. The first red Naphthol AS pigment was synthesized in 1912. Figure 1-7 shows a general structure of a numerous azo pigments<sup>4</sup>.

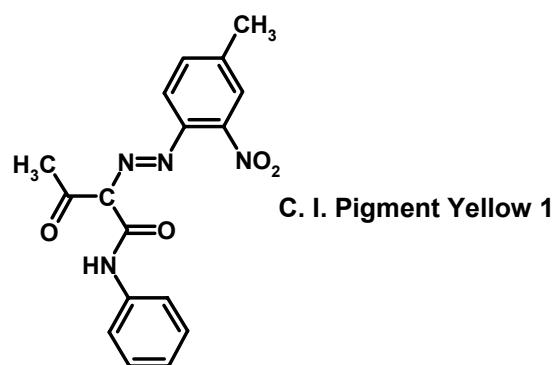


Figure 1-6: Chemical structure of Hansa Yellow.

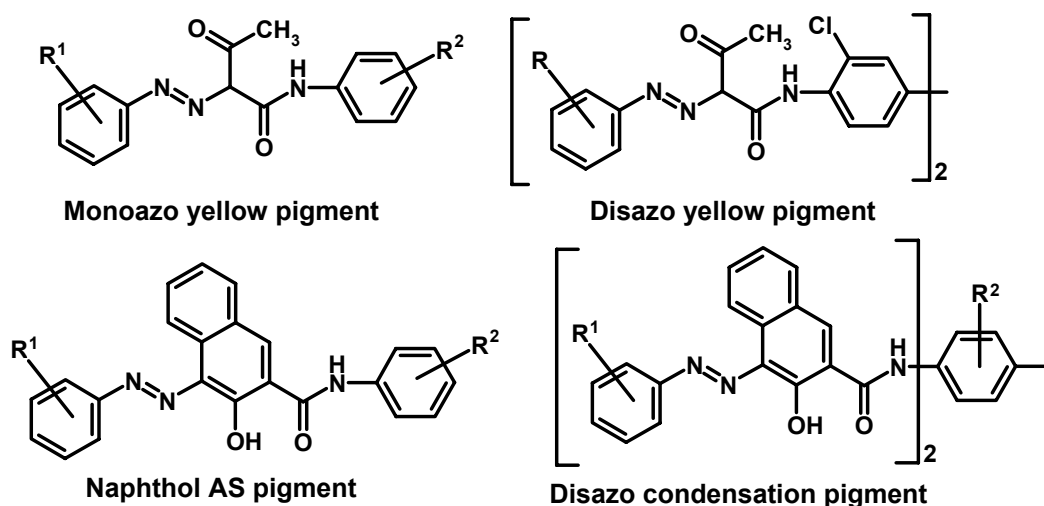


Figure 1-7: General structure of mono- and disazo pigments:  $R$ ,  $R^1$  and  $R^2$  represent various substituents.

In 1928, the discovery of copper phthalocyanine (s. Figure 1-8a), a blue pigment, which offers excellent intensity and brightness comparable to many inorganic pigments, stimulated the development of a range of high-performance organic pigments<sup>4</sup> such as quinacridones, isoindolines, perylenes, diketopyrrolo pyrroles and anthraquinones which are shown in Figure 1-8b-f.

The study on many high-performance pigments surface modifications as well as the application of polymeric dispersants to improve rheological characteristics of modern high-solids solventborne pigment dispersions have been reported<sup>5</sup>. In addition, surface modification of pigments and the use of compatible polymeric dispersants have made an important contribution toward lowering paint viscosities<sup>6</sup>. The surfaces of the pigments such as anthraquinones (AQ), and diketopyrrolo pyrroles (DPP) were treated with an anchor group containing acidic moiety<sup>6</sup>. After surface treatment, they were dispersed in the polymeric dispersants such as tertiary amino functions of aromatic or non-aromatic character on a polyurethane chain. It was shown that the combination of a surface modified pigment with an appropriate polymeric surfactant could inhibit the reagglomeration and subsequent flocculation of individual pigment particles. As a result, the surface treatment of the pigments show a significant lowering effect of the viscosity compared to unmodified pigment.