25 years of ColorMatic lenses

In 1986, 20 years after the first photochromic mineral lens, Rodenstock launched the first generation of photochromic plastic lenses, Perfalit ColorMatic. **Dr Herbert Zinner, Dr Herbert Schuster, Dr Udo Weigand** and **Dr Werner Müller** look back on the continuous improvement of these intelligent, light-sensitive lenses

The history of plastic photochromic lenses is one of the improvement of the chemistry behind the effect of darkening and fading of highly specialised dye molecules. The basic principle of the photochromic effect has not changed over the past 25 years.

A colourless organic molecule is excited by UVA irradiation (Figure 1). As a result, a certain chemical bond of the molecule is broken and the accompanying structural and electronic change shifts the absorption spectrum into the visible region – the molecule is now coloured ('activated'). The molecule relaxes back to the colourless ('inactivated') state predominantly by thermal rearrangement ('fading').

Many chemists have invested a lot of brain power and laboratory work over the past 25 years to optimise the highly sophisticated structures of the organic molecule, both inactivated and activated. Furthermore, the environment for these molecules (that is the plastic material) which has an important influence on the performance of the photochromic lens, has been similarly optimised.

We will now take a closer look at these developments over recent years.

Perfalit ColorMatic – 1986

Rodenstock launched the first Perfalit ColorMatic in 1986. The state-of-the-art photochromic dye was a quite simple Indolino-Spiro-NaphthOxazine (ISNO) exhibiting a blue colour in the activated state (Figure 2). For tinting the regular CR39 material with the photochromic dye, Rodenstock used a thermal transfer tinting method.

To effect a neutral colour in the activated state, the lens had a permanent brown tint of 25 per cent absorption. Exposed to UV irradiation (50kLux @ 23°C) the lenses darkened up to 60 per cent absorption with a blue/grey hue. But this first generation of photochromic lenses had – compared to mineral photochromic materials – a major disadvantage: fatigue resistance.

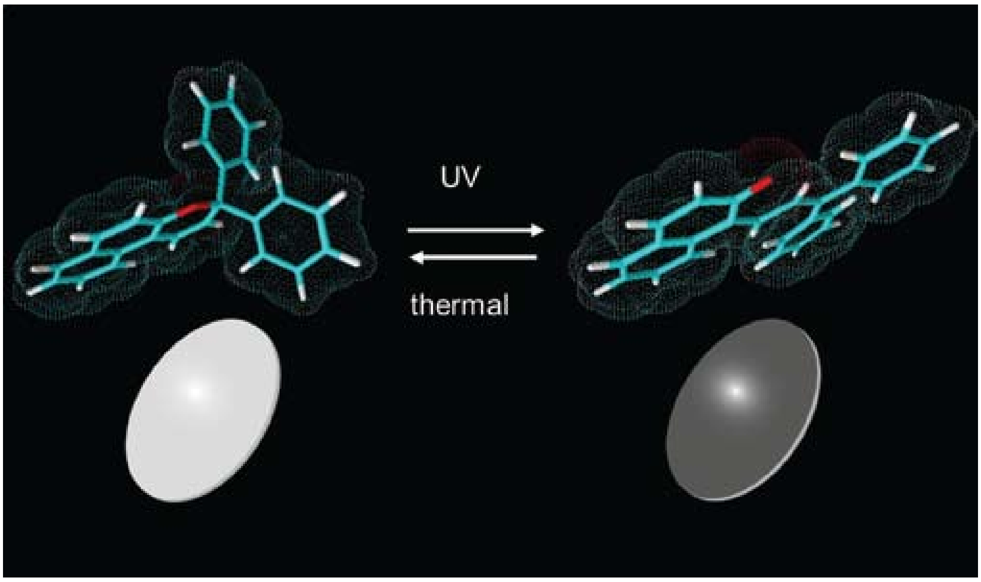

Figure 1 UV and temperature alter molecular structure

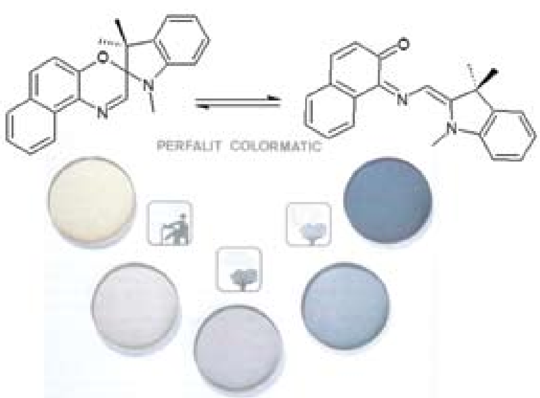

Figure 2 ISNO activation to a blue lens

Figure 3 Three Photocolors

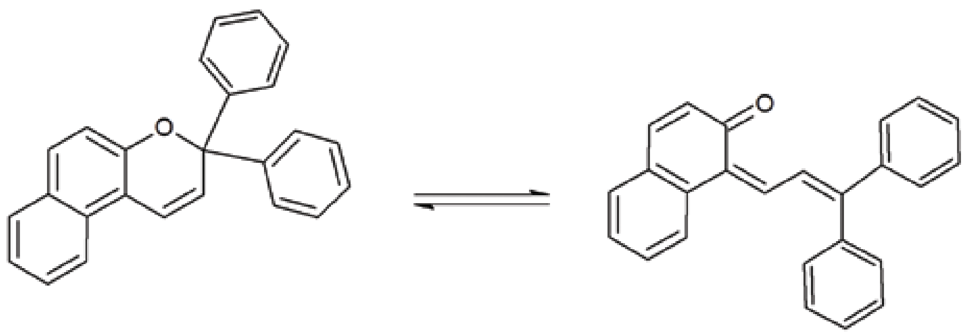

Figure 4 Structure of naphthopyranes

This is the loss of absorption of the activated state over time and this was still poor.

Compared to the inorganic colour pigments of mineral photochromic lenses, organic dyes like ISNOs are less stable to light, especially in combination with oxygen. The near-the-surface position of the molecules also reduced the lifetime. AR coating was mandatory to stop the penetration of oxygen and to guarantee an acceptable degree of fatigue resistance.

Looking for colours

After the launch of Perfalit ColorMatic, chemists tried to modify the chemical structure of ISNOs to achieve different colours for the activated state. A diversity of modified structures was synthesised, covering a colour range between violet and green (Figure 3). In 1988 Rodenstock used this range of colours and the same imbibing method to launch three fashion colours called Photocolor.

But a real neutral grey colour of the activated state photochromic molecules with a colour range from yellow to orange (red) was still missing. At that time the molecular class of naphthopyranes entered the fray and changed the photochromic landscape. Depending on the molecular structure of the naphthopyranes (Figure 4), yellow to orange colours were now possible and the race for a neutral dark colour for the activated state was now on.

But having a range of colours is only one aspect of the quest for the perfect photochromic lens. The photochromic organic molecule must fit into the matrix of the plastic material. If there are different colour molecules they all have to be incorporated into the plastic material in the right concentration – something well known from normal plastic lens tinting. This was the time when PPG began to modify normal CR39 for Transitions lenses.

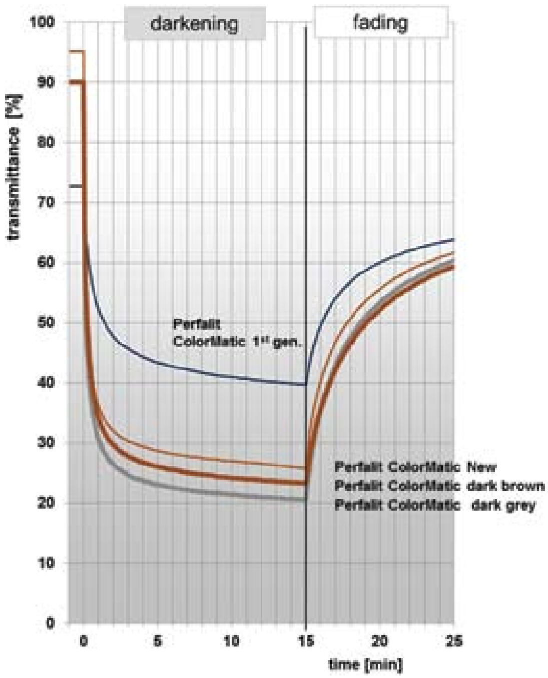

Figure 5 ColorMatic transmittance curves

Rodenstock took a different path and changed from surface tinting to mass tinted lenses. But neither CR39 nor high index plastic materials like MR8 (n=1.60) or MR10 (n=1.67) were usable for this method because in all these systems the photochromic dyes are attacked by the monomers or the polymerisation initiators. Using tailored acrylate-based monomer mixtures, the photochromic molecules could be dispersed 'in mass'. Employing a sophisticated combination of initiators and a polymerisation process Rodenstock managed to produce high quality photochromic mass tinted lenses. A distinctive advantage of this process is the homogeneous distribution of the photochromic dyes throughout the whole lens – scratches on the surface do not result in a local defect in photochromic performance.

Perfalit ColorMatic New - 1995

Using this technology, Rodenstock launched ColorMatic New in 1995. This photochromic lens was based on a mixture of seven photochromic dyes, spiroxazines as well as naphthopyranes. This combination of dyes was chosen to create a brown colour for the activated state.

Compared to the first generation, the lens was considerably improved in all important photochromic criteria. The transmittance of the inactivated state was improved from 75 to 90 per cent and even 95 per cent with AR-coating. At the same time the absorption of the activated state was raised from 60 to about 75 per cent. The temperature dependency of the degree of darkening was improved owing to the use of a new generation of photochromic dyes (Figure 5).

The photochromic characteristics of ColorMatic New were designed for European customers, meaning that a major focus was set on achieving the highest possible degree of transmittance of the inactivated state combined with a reasonable fading speed at normal temperatures.

Looking at lenses

To respect concerns of markets with demand for darker photochromic lenses Rodenstock in the following years launched ColorMatic Dark in grey/brown, ColorMatic Superdark grey and the first green photochromic lens SunMatic. The latter was the first green photochromic sun lens with a permanent tint of about 25 per cent absorption.

The successful production of a brown photochromic lens with a high degree of transparency in the inactivated state was the first step. Using different photochromic dyes requires exact matching. To ensure colour stability during the whole process of darkening and fading the speed has to be the same for all dyes. Additionally the dyes have to show similar fatigue resistance during the lifetime of the lens.

Perfalit ColorMatic Extra – 1999

The chemists managed to synthesise naphthopyranes with violet to blue colours in the activated state with apparently little change in the chemical structure (Figure 6). An advantage of this new type of photochromic molecule is a broader absorption peak of the activated state. Accordingly the number of dyes necessary to produce a neutral brown or grey colour could be reduced. Based on this innovative research, Rodenstock launched ColorMatic Extra, the third generation of Rodenstock's photochromic lenses, in 1999. The product was a completely new design. Not a single dye in this product was the same as those of the second generation products and, to give an additional improvement in darkening and fading speed, the polymer material was also adapted to the requirements of the photochromic dyes. The result was a tremendous improvement in absorption when fully activated, in fading speed, colour stability and fatigue resistance.

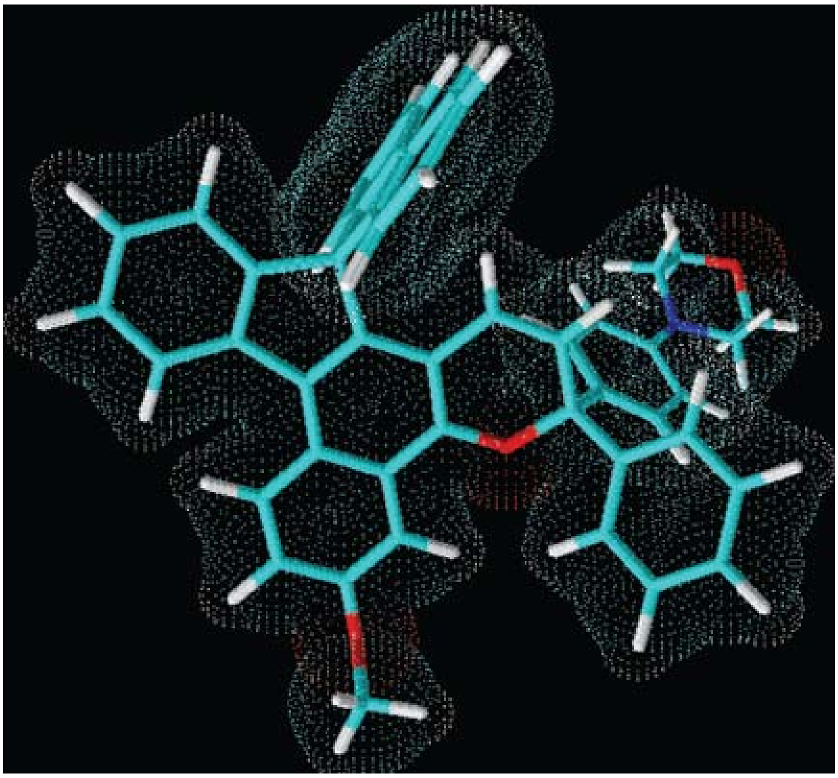

Figure 6 ColorMatic Extra photochromic molecule

Compared to the grey lens of the second generation (ColorMatic Dark grey) the ColorMatic Extra grey lenses showed an at least 5 per cent higher absorption level of the activated state at intermediate temperatures (Figure 7). At the same time the lens exhibited a significantly faster speed of fading, needing only three minutes to reach the same level of ColorMatic Dark grey which of course started from a lower absorption level. We all know that the speed of the first few minutes of fading is the most important period for the customer when switching from outdoor sunlight conditions to indoor conditions. Showing a uniform constant grey colour during the complete process of darkening and fading, the colour was practically temperature independent. Again compared to the second-generation products the progress in quality was impressive – for example a 30 per cent higher residual performance after the standard fatigue test (100h irradiation with a strong xenon lamp) compared to ColorMatic Dark grey (Figure 8).

Further development resulted in a dye composition with a very high absorption at wavelengths <400nm. A high absorption in this region leads to an optimal efficiency of 'harvesting' the activating UVA rays. On the other hand, an absorption >420nm leads to a perceptible permanent yellow hue of the inactivated state of the photochromic lens. The skill of an organic chemist is to design and then synthesise photochromic molecules with an optimal absoption <400nm and a minimum absorption >420nm. So ColorMatic Extra has additional absorption, additional photochromic efficiency, additional UV protection, but no accompanying yellow hue.

So where to go now? We always have to be aware that the primary function of photochromic lenses is of course to solve optical needs. For this reason the customer wants thinner lenses and the easiest way to realise thinner lenses is a higher refractive index. Second- and third-generation Rodenstock ColorMatic had a refractive index of 1.52. The aim was to raise the refractive index of the next product while retaining fatigue resistance and lower production costs. Moreover, improved mechanical properties of the lenses were sought. The developers created the next generation based on a polymer with a refractive index of 1.54.

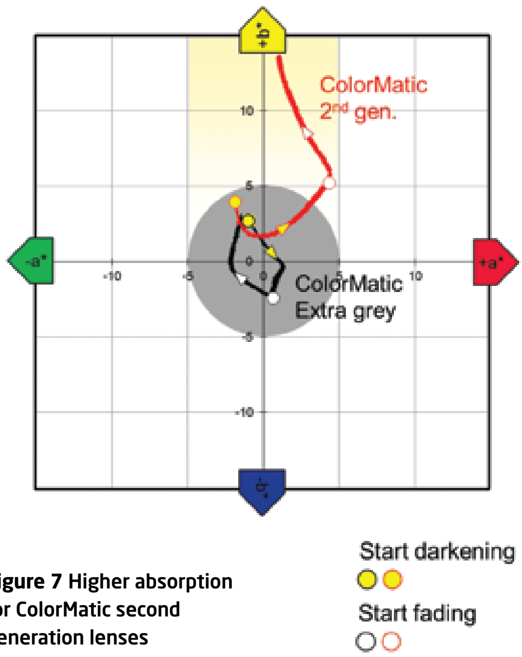

Figure 7 Higher absorption for ColorMatic second generation lenses

Further ColorMatic products

In January 2006 Rodenstock introduced the new mid-index lens ColorMatic 1.54 in brown and grey. The transmittance of the inactivated state was improved to more than 92 per cent (with AR coating). Compared to competitor products at that time, fading in the most important first minutes was significantly faster. The new photochromic dyes guaranteed 100 per cent UV protection.

But there still was a need for photochromic lenses with yet higher refractive indices. Photochromic low- and mid-index polymers are usually either methacrylate-based polymers with homogeneously dispersed photochromic dyes ('in mass') or derivatives of CR39 which are then imbibed with photochromic dyes ('on surface'). For these types of polymers there is no way to attain a refractive index of 1.6 or higher. High-index plastic lenses are based on completely different chemical polymers and all attempts for mass tinting or imbibing these types of lenses failed. Transitions Quantum was the first product applying a photochromic coating on high-index materials.

Rodenstock engineers focused on applying a thin photolacquer onto a standard high index lens. In 2006 Perfalit ColorMatic 1.67 was launched, with Perfalit ColorMatic 1.6 following one year later. Both lenses were in brown and grey options.

From a photochromic standpoint the biggest advantage of the new high-index product was its distinctively faster fading speed compared to the 1.54 product. This was due to the softer photolaquer matrix and its reduced inhibition of the activation cycle of the photochromic molecules. With 85 per cent absorption of the activated state at 23°C, Perfalit ColorMatic 1.67 was not the darkest lens in the market, but featured superior fading speed after two minutes.

Specially designed ColorMatics

Most customers think only of grey and brown photochromic lenses. But there were attempts to attract a younger market selling additional colours eg Transitions Splitz.

Eighteen years after Photocolor fashion colours, Rodenstock launched ColorMatic 1.54 green in April 2006, soon followed by the high-index version ColorMatic 1.6 green. To enhance contrast, certain permanent tints were employed: first an orange colour in the inactivated state with 40 per cent absorption (with AR coating) and second a green colour with 50 per cent absorption.

ColorMatic IQ

The first photochromic high index lenses were not perfect in all photochromic criteria. The transmittance of the inactivated state and the fatigue resistance were still on a lower level compared with the respective 1.54 products and the colour during fading tended to a yellow hue.

Improvement on these aspects was a high priority during the development of the next generation of photochromic high index lenses, named ColorMatic IQ. ColorMatic IQ is available with refractive indices 1.6 and 1.67 and has just been launched on the market.

Compared to the former ColorMatic 1.6, the transmittance of the inactivated state (with AR coating) is improved to 92 per cent without the slightest yellow hue. During the whole fading period no yellowness is observable. ColorMatic IQ is also 50 per cent faster than its main competitor during the first two minutes of fading (after full activation according to norm) and after three minutes of fading Colormatic IQ exhibits 20 per cent higher degree of transmittance (Figure 9).

The chosen absorption level of the activated state is a careful balance between contradicting requirements: Colormatic IQ gets dark enough in sunny conditions on a hot summer day but not too dark, especially in hazy conditions on a cold winter day. With the launch of ColorMatic IQ Rodenstock decided to introduce a new set of modern brown, grey and green colours in their activated state.

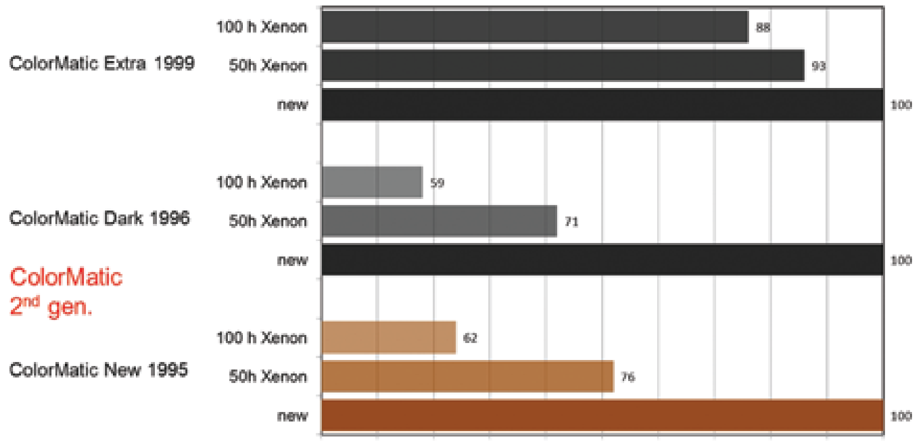

Figure 8 Residual performance after irradiation with xenon lamp (%)

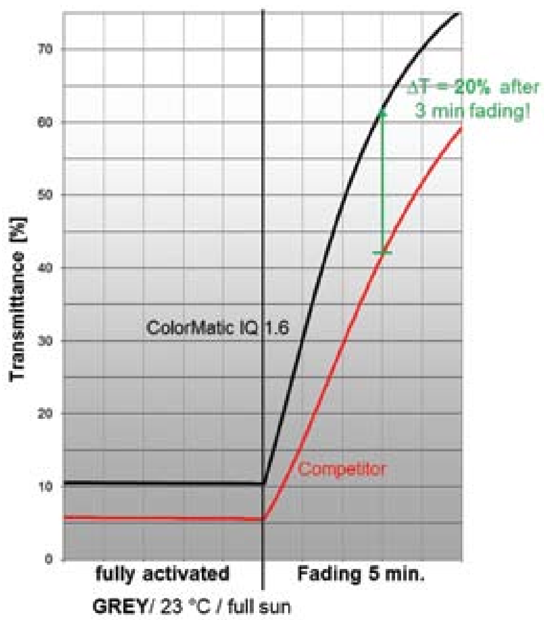

Figure 9 Comparison of phototropic performance at 23°C/50klux with HC/AR

Summary and outlook

The journey through 25 years of photochromic plastic lenses by Rodenstock is a story of continuous research and improvement. A lot of the early problems have been overcome; photochromic plastic lenses have easily replaced their mineral counterparts during this period. The latest photochromic plastic lenses exhibit a minimal absorption in the inactivated state accompanied with perfect UV protection, a fast fading speed, a remarkable colour stability and excellent fatigue resistance.

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