The Chemistry & Physics of Special Effect Pigment & Colorants "What They Are & How They Are Used"

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INTRODUCTION:

Anything that does not fall under any other designation can be grouped under Special Effect Colorants & Pigments heading. What this presentation will attempt is to give some of the history, some chemistry and physics and also some suggestions as to how and where these pigments can be used.

Special effect colorants & pigments that we will discuss can be divided into the following groups.

- 1. Daylight Fluorescent Colorants
 - a. Thermoset
 - b. Thermoplastic
 - c. Dispersion
- 2. UV & IR Fluorescent Colorants
 - a. UV
 - b. Optical Brightening Agents
 - c. IR (anti Stokes)
- 3. Phosphorescent Pigments
 - a. Zinc Sulfide based types
 - b. Alkaline Earth Aluminate types
- 4. Optically Variable Pigments
- 5. Photochromic colorants
- 6. Thermochromic colorants

WHAT MAKES THEM SPECIAL?

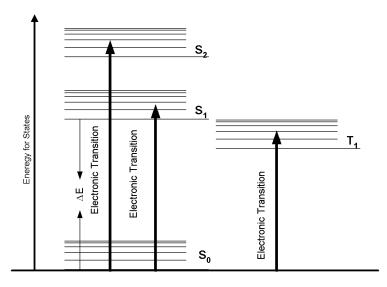
Each Specialty Colorant has a specific attribute that makes them stand out when compared to regular colorants and pigments.

In order to be able to describe these attributes first we must give some definitions as to what we mean:¹

LUMINESCENCE:	Fluorescence and phosphorescence;
LUMINESCENT COLORANT:	A material which emits light (visible, IR or UV) upon
	suitable excitation, without becoming incandescent;
EXCITATION:	A means of causing a luminescent colorant to emit light;
FLUORESCENCE:	The emission of light by a luminescent pigment under
	excitation (<i>e.g.</i> daylight fluorescent);
PHOSPHORESCENCE:	The emission of light by a luminescent pigment after
	excitation has ceased (<i>e.g.</i> glow-in-the-dark);
THERMOCHROMIC	Reversibly altering color upon exposure to a heat source;
PHOTOCHROMIC	Reversibly altering color upon exposure to a UV rich
	light source

There are many forms of energy which selected luminescent pigments can absorb and convert to luminescence, *e.g.* radioactive (**radioluminescence**); X-ray (**Roentgenoluminescence**); cathode ray (**cathodoluminescence**); mechanical (**triboluminescence**); electrical (**electroluminescence**); heat -after previous storage of energy (**thermoluminescence**); and Ultraviolet (UV) visible and Infrared (IR) (**photoluminescence**).

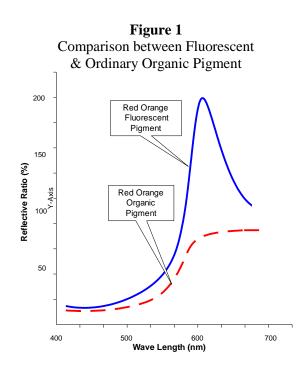
The phenomenon of luminescence can be explained by the Energy State (or Jablonski diagram).



When a luminescent pigment molecule is excited by light energy, they are excited to higher Singlet energy states, which then revert to their original ground state by emitting a portion of their absorbed energy. If decay is directly from S_2 to S_0 then fluorescence occurs, if the energy is dissipated via the triplet state ($T_{1 \text{ or } 2}$), then phosphorescence occurs.

FLUORESCENT COLORANTS:

Fluorescence is a phenomenon that occurs when a substance absorbs radiation of a certain wavelength, or group of wavelengths, and re-emits photons of a different wavelength.

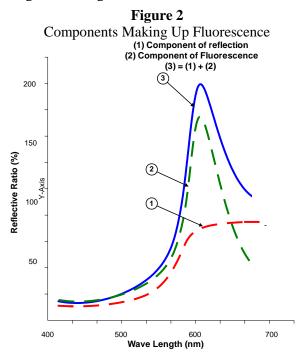


When certain compounds absorb light, an electron is excited to a higher vibrational energy state. The molecule then loses its excess of vibrational energy by collisions or by emitting a photon in the infrared or microwave bands and falls to the lowest vibrational level of the energy state. In addition, almost all molecules occupying an energy state higher than the second undergo internal conversion and pass from the lowest vibrational level of the upper state to a higher vibrational level of a lower state that has the same energy. From there, the molecules again lose energy until the lowest energy level of the first excited state is reached. From this level, the molecule can return to any of the vibrational levels of the ground state, emitting its energy in the form of fluorescence. Typically, molecules that display fluorescence are of two types organic compounds with a high degree of conjugated unsaturation and extended p- cloud

structure, or inorganic compounds where it is relatively easy to promote an electron to a higher vacant energy level (usually a d- or f- level), and the molecule may be excited to a higher vibrational and rotational energy state. The spectrum of the emitted light is called the emission spectrum. Due to the conservation of energy, the emitted light is almost at a longer wavelength.

This discussion will only address these cases. The difference between the excitation and the emission wavelength is called the Stokes Shift. Typically, the Stokes Shift for organic compounds is much larger than for inorganic compounds and also usually occurs at longer wavelengths.

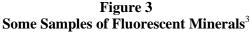
The reflectance of an object determines the color. In a non-fluorescent molecule, photons are still absorbed but they immediately drop back to the original energy state, dissipating the energy in the form of heat or simply emitting a photon of equal wavelength. The result is a typical absorption spectrum, since absorption is merely the $\log (1/R)$. If there are molecules in the colorant mixture that fluoresce, the resulting spectrum is a combination of a number of factors, including the reflectance of the non-fluorescing materials, the absorbance of the fluorescent material due to the excitation of electrons to a higher energy state, and the emission spectrum of the fluorescing material. Truly a mess to interpret since both the absorption and fluorescence depend on the spectral power distribution in the illuminant used.



Fluorescence is also not uncommon in nature. Many organic and inorganic species fluoresce to some extent. Most soils containing humus fluoresce, as do many bacteria. Fluorescence is common in minerals as well. Many science museums will usually include a display of minerals illuminated by both tungsten lamps and black lights (UV source) to demonstrate this phenomenon. Almost all uranium compounds commonly found in granite fluoresce as do many zinc, cadmium, and copper ores.²



Fluorite

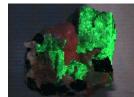




Fluorite under UV



Willemmite



Willemmite under UV

DAYLIGHT FLUORESCENT PIGMENTS:

Daylight fluorescent pigments are an original American invention. In the 1930's, Bob and Joe Switzer experimented with ways of combining certain dyes and resins that produced colors far brighter than normal and that had the unique effect of "glowing" under ultraviolet or black light.

Initially, these new colors and effects found their way into magic shows, stage shows, and movie promotion posters. In 1936, they became associated with a firm in Cleveland, Ohio, which produced the movie posters and moved to Cleveland from California.

During WWII, their focus was diverted to the manufacture of bright signal panels as used by the army. After the war, this technology was utilized in outdoor billboards where the message "jumped off the boards."

Fluorescent pigments are solid dye solutions in polar resin carriers. Fluorescent dyes in their undissolved state do not fluoresce. Once these dyes are dissolved in a thermoplastic or thermoset carrier resin and are ground into a fine powder, they become fluorescent pigments.

Only a few fluorescent dyes that are commercially available can be made into pigments. Some of the most important dyes used are based on Rhodamine B (invented in 1877). The most common fluorescent dyes used are shown in Table I.

Basic Violet 10	Basic Yellow 40				
Basic Violet 11	Solvent Yellow 135				
Basic Red 1	Solvent Yellow 160:1				
Acid Red 52	Solvent Yellow 43				
Solvent Yellow 44					

 Table I

 Fluorescent Dyes used in Manufacturing Daylight Fluorescent Pigments

There are different types of carrier resins for daylight fluorescent pigments.

Thermoplastic Pigment (Melamine Formaldehyde Type)

One of the oldest types of carrier resins is based on PTSA (Para Toluene Sulfonamide) – melamine – formaldehyde, which is fully condensed resins and melt at a range of about 115-135°C, are clear, brittle and easily pulverized into a pigmentary form. (used in printing inks)

Thermoset Pigment (Melamine Formaldehyde Type)

These types were the next to be developed. Through post curing and some chemical modification of the PTSA-MF resins solvent resistance was increased and softening temperature was raised to 175°C. (used in printing inks)

Thermoset Pigment (Benzoguanamine Formaldehyde Type)

A newer type, where the melamine component of the PTSA-MF is replaced by benzoguanamine. This results in a spherical particle size rather than ragged edges. (**used in printing inks**)

Thermoset Pigment (Benzoguanamine Formaldehyde Type)

These are specifically developed for plastics in order minimize the plating tendency of all other types. They contain only benzoguanamine formaldehyde type matrix. (**may be used in printing inks**)

Thermoplastic Pigment (Polyamide Type)

These types were developed for use in plastics. They are based on aliphatic diamines and isophthalic acid with melting points between 110° C to 150° C depending on the intended application.

Thermoplastic Pigment (Polyester Type)

These also were developed for use in plastics. They are based on polyfunctional glycols and phthalic anhydride. They have lower softening points (around 90°C) and are considered less heat stable than PA types. They do not contain any formaldehyde.

Thermoplastic Pigment (Vinyl or Acrylic Type)

These are mainly used for calendered vinyl and the matrix is based on PVC or an acrylic resin. They do not contain any formaldehyde and display very high color strength.

Aqueous Dispersions (Acrylic Type)

These are a newer development in fluorescent pigment manufacture and are specifically designed for printing and writing inks. They are manufactured by adding fluorescent dyes into acrylic monomer and then polymerizing, thus creating colored latex particles (globules). They are formaldehyde free and have a very fine particle size (sub micron), which is very suitable for ink manufacture. **(used in printing inks)**

UV FLUORESCENT PIGMENTS:

Inorganic Fluorescent Pigments (IFP) are further distinguished from daylight organic fluorescent pigments by the fact that most are either colorless or have very pastel colors under daylight, but when excited by UV radiation, they fluoresce in relatively bright colors. The excitation energy can either be short or long UV. The visible color of these inorganic pigments is entirely due to emitted radiation and they are additive colors. Thus, a blend of equal parts of a green glowing and a red glowing pigment results in a yellow glowing pigment. These chemicals encompass a wide variety of luminescent chemicals such as lamp, TV and CRT phosphors, but this discussion will cover only ones that are used in

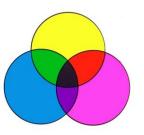


"coloration" of inks, coatings, plastics, and similar applications. With organic compounds, luminescence is essentially based on localized electronic systems within the organic molecules. Whereas with inorganic compounds the luminescence is determined by their

lattice structures and thus their luminescence is altered or disappear totally when their crystal structure is altered in any way (melting, decomposing or breaking).⁴

The classical IFPs have been based on the Zinc

Figure 4B Subtractive Colors



Sulfide and Zinc Cadmium Sulfide. These Inorganic Fluorescent Pigments (e.g. [Zn, Cd]S doped (activated) with Silver, Copper, or Manganese) are today considered "toxic" (Because of their Cadmium content). The activator type and amount used determines the color of the fluorescence. For example, when copper is used as the activator the color can be varied from green to deep red, whereas when silver is used, the fluorescence color ranges from deep blue to deep red.

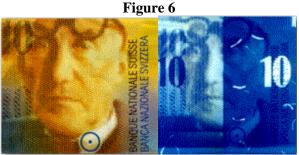
In the past, another disadvantage of IFPs was their particle size. All IFPs depend on their crystal structure in order to emit light. When they are ground to smaller particle sizes in the ink vehicles, they lose their potency. Thus, these early IFPs were not suitable for printing inks other than silkscreen, or in very rare instances gravure, because of their large particle sizes. In any case, there are no known manufacturers of such pigments left today.

Therefore, a special range of inorganic luminescent pigments (some of them based on Rare Earth elements and some having quite complex crystal structures) that have been specially surface treated for ease of printing, have been developed to satisfy the printing industry's needs. These pigments have found use, especially in the security printing industry, and they have been designed with this specific industry's needs in mind.

Basically, these pigments are composed of a microcrystalline host (or matrix) based on rare earths and an activator, i.e. a small amount of intentionally added impurity atoms distributed in the host crystal. Some of such matrices are: oxides, sulfides and oxysulfides of rare earth elements, aluminates of alkali earth metals, etc.

An important use of these pigments is in document security applications. One has to take into consideration the security printing industry's stringent requirements for the pigments that it would use. In addition to being as "forgery proof" as possible, the end product should also pass other quality and durability requirements. Some of these are:

- The pigment should possess excellent light fastness;
- It must have superior rub (dry & wet) fastness;
 Its fastness to various solvents and chemicals must be excellent, i.e., ethyl acetate, ethanol, acetone, trichloroethylene, benzene, xylene, bleaching solutions, caustic soda, acetic acid, hydrochloric acid, perspiration, soap, detergent, etc.



Under normal light Under UV light

Figure 5 Under normal light





♦ It must have a particle size small enough to be printable with all printing processes.

These requirements are so stringent that even most color pigments cannot meet them, let alone common daylight fluorescent ones.

Examples of such prints are shown in Figures 5 & 6. The same design is shown both under normal light and UV light.

When using UV Fluorescent pigments you have to keep in mind their shortcomings. These can be summarized as:

- **Particle size**: Average particle size is larger than organic pigments, *i.e.* sub-micron versus larger than 2 4 microns. They should also not be ground too fine as their afterglow is dependent on their crystal structure. Once this is broken, they do not glow.
- Abrasiveness: As they are based on inorganic molecules (some are even based on aluminates) they can be quite abrasive. Therefore you should be careful with damage on gravure rolls and offset plates.
- **Color Strength**: As their color formation is dependent solely on the fluorescent component, you might have to use more than normal quantities in order to be able to get bright enough colors.
- Additive Color Concept: Remember that these colors are additive, a mixture of Red, Blue and Green results in a WHITE, and not a black. Therefore if you are thinking of your prints to be true to their intended colors, you have to use different filters.

A subset of the UV Fluorescent pigments are pigments that are used in tagging postage stamps. Most of these pigments are excited by short wavelength UV light (around 254 nm). There are both organic and inorganic types. The organics are either based on salicylic aldazines or substituted benzooxazinones (used in Canadian, German and Italian postage stamps). The inorganics are based on ZnSiO₃:Mn (as used in the US and Hong Kong Postage stamps).

OPTICAL BRIGHTENING AGENTS (OBA):

Optical Brightening Agents (OBA), a.k.a. Fluorescent Brightening Agents (FWA), are a particular class of organic compounds that have very specific fluorescent properties. They have excitation maxima in the very near UV (340-400 nm) and emit in the 430-460 nm wavelength ranges.⁵ The major uses of these products are for hiding the yellowish tint of paper, textiles, coatings and plastics, by giving them a bluish tint. Typically their chemistry is based on the stilbene molecule and are modified to enhance solubility and uptake depending on the substrate in which they are used.

Another use for these products is printing invisible markings in security applications, similar to UV Fluorescent pigments. (Most probably the sample in Figure 6 has been manufactured using an OBA.)

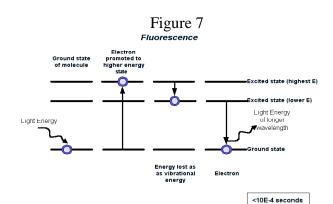
IR FLUORESCENT (Anti-Stokes) PIGMENTS:

Another class of specialty pigments that are not known much in industry is the IR Fluorescent or Anti-Stokes Pigments. The Stokes Law states that when a molecule is excited by a source of certain wavelength, the resulting color output is of a higher wavelength. Examples are excitation by UV light that results in various visible colors that are of longer wavelengths. But IR Fluorescent pigments do not follow this law, they are excited by IR energy, and either emit in the visible region or in the IR region but at a shorter wavelength.

These products can also be used in printing inks by taking the same precautions as in IFPs. In order to detect them special near IR lasers or LED's are needed.

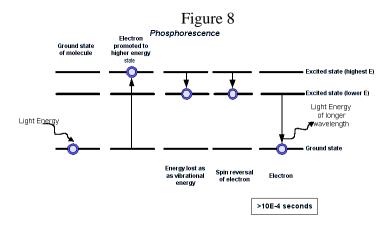
PHOSPHORESCENT PIGMENTS:

Phosphorescence is similar to fluorescence in as much as it is a phenomenon that occurs when a substance absorbs radiation of a certain wavelength, or group of wavelengths, and re-emits photons of a different wavelength. The difference is in the emission time. As a rule of thumb, if emission stops after the excitation source has been removed, then the resulting luminance is called fluorescence, if emission continues (so called "afterglow") then it is called phosphorescence.



The reason for the afterglow can be explained with the help of Figures 7 & 8. In fluorescence the absorbed energy is dissipated by first going to a lower energy state and is lost as vibrational energy. Time lag is also very short ($<10^{-4}$ sec.). When the excited electron also goes through a spin reversal and can stay longer in that excited state, resulting luminance is termed phosphorescence. Time lag is > 10^{-4} sec.

There are also phosphorescent minerals, but their phosphorescent intensity is very low and actually beyond the capabilities of the human eye to detect. The first recorded observation of inorganic luminescence by V. Cascariolo ca. 1603 was also phosphorescence⁶. One way of observing this very low phosphorescence is to place them in front of a photographic film, after being activated by a suitable light source, and record the image developed on the film.



The origin of non-radioactive synthetic phosphorescent pigments goes

back to the late 1930's, when it was found that Zinc Sulfide when doped with Copper (in the order of 0.01%) could become phosphorescent. The early use of these pigments was in military applications where they were used to illuminate the dials of instruments, clocks and watches for night viewing. One problem that they were not commercialized much, was that these early pigments did not have enough afterglow power to be of much use in such applications.

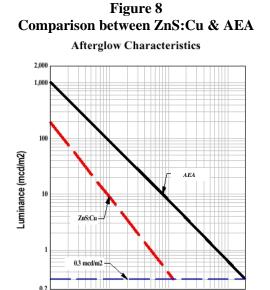
Later on, through improvements in their manufacturing process, Zinc Sulfide:Copper doped (ZnS:Cu) type phosphorescent pigments acquired afterglow characteristics that were strong enough to be usable in safety signage. These pigments had a green afterglow with a peak at 520 nm.

These pigments were (and are still) also used in toys, novelties, and textile printing. However their main deficiencies were that:

- their particle size was too large for printing except silk screen (av. 25 μm);
- in order to obtain decent afterglow, a very thick layer containing a very large amount of pigment was required;
- Afterglow is particle size dependant, larger particles have brighter afterglow.

In 1993, a new class of phosphorescent pigments based on rare earth alkali earth metals *AEA*⁷ was invented in Japan by researchers at Nemoto & Co., Ltd of Tokyo. These pigments at equal loading had 10 times the afterglow and 10 times the brightness of classical phosphorescent pigments.

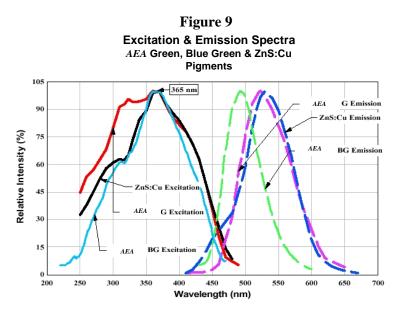
The invention and further development of this new class of pigments opened new possibilities in a multitude of ways, because an acceptable level of afterglow was possible by using less pigment and the afterglow time had increased tremendously.



10

5

These *AEA* pigments were also manufactured in a blue green (aqua) and violet afterglow colors. Figure 9 shows the excitation and emission curves of ZnS:Cu and green and blue green emission *AEA* pigments.



These newly invented pigments initially had their own problems, mainly:

100

50

Time (minutes)

500 1.000 2.000

- They had large particle sizes : > 20 microns(developed for the plastics industry);
- They were hard and abrasive (6.8-7.0 on the Mho scale);
- They lost their after glowing capability when moist (while in powder form).

Recent developments have solved most of these problems and now can be used in gravure and flexographic printing inks. A sample made using *LumiNova*[®] FF by flexo printing is shown in Figure 10

Figure 10



Still when using these pigments the following precautions should be taken.

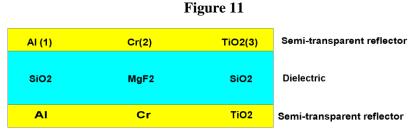
- First all AEA pigments are not created equal. Ask for the printing ink types.
- Do not grind, just stir in to mix. The correct type will already have a much smaller particle size distribution;
- If possible do not use any metal impellers. Due to the abrasiveness of these pigments darkening of the color occurs;
- Do not use water-based resins. Or if you are forced into using such a system, add the pigment just before printing. Keep the runs small. Accept the fact that the afterglow will be diminished.

OPTICALLY VARIABLE PIGMENTS:

Optically Variable Pigments (OVP®)⁸ show angle-dependent color and lightness effects which are based on reflection, interference and absorption phenomena of visible light in pigmentary multilayer systems.⁹

Optically Variable Pigments' color changing ability is based on a physical phenomenon known as the Fabry Pérot interference principle which was first observed in 1897 (this method was originally used for determining the wavelength of light).

OVP®'s are multi-layer films of semi-transparent reflector (metals) and dielectric materials. These can be made of three layers as shown in Figure 11, or

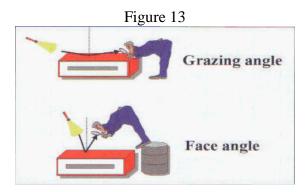


Note: (1) DuPont - USP 3,438,796; (2) Flex Products - EP 395,410; (3) Merck - WO 93/08237

a second type which has a core of reflective material which in turn is covered by a symmetrical system of weakly refractive and partially reflective layers, for a total of five layers. This type is shown in Figure 12.

АІ	Cr	MoS2	Fe2O3	Fe2O3	MoS2	Fe2O3	Partially Reflective
SiO2	MgF2	SiO2	SiO2	SiO2	SiO2	SiO2	Low Refractive
AI	AI	AI	AI	Fe2O3	Mica/ oxide	Mica/ oxide	Inner Reflector
SiO2	MgF2	SiO2	SiO2	SiO2	SiO2	SiO2	Low Refractive
АІ	Cr	MoS2	Fe2O3	Fe2O3	MoS2	Fe2O3	Partially Reflective

In this second type of $OVP^{\textcircled{0}}$ the center "inner reflector" layer is usually Aluminum, and the "low refractive" layers can be either SiO₂ or MgF₂ or Fe₂O₃; and the partially reflective" outer layers can be Al (DuPont - USP 3,438,796), Cr (Flex Products - USP 4,434,010), MoS₂ (BASF – USP 5,401,306), Fe₂O₃ (BASF – EP 708,154 & BASF DE 195 25 503)¹⁰. None of these layers have any color of their own, but when they are intimately put into contact with each other, they give rise to brilliant colors because of the components selective destructive and constructive interference as light reflects off the interfaces.¹¹



green to blue and; gold to green. Usually they are printed with intaglio presses with an engraving depth of 50 to 70 microns with a regular pattern.¹³

The pigments are usually 1 micron in total thickness and the tolerances are very tightly controlled. See Figure 14¹⁴

Some examples of OVP® prints can be seen in the currency samples either in your pocket (look for the new \$100, \$50, \$20, \$10 and \$5 bills) or as shown in Figure 15. OVP®'s whole color play cannot be seen with the usual flop movement that is characteristics of metallic pigments. Therefore two extreme illumination and observation positions, face angle and grazing angle are necessary to see all the color shades of the pigments as shown in Figure 13.¹²

Changing the thickness of the interference layers changes the observed colors. The usual shifts are magenta to green;

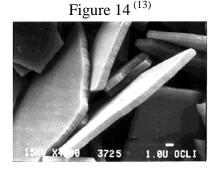


Figure 15

Various samples of OVPTM using prints



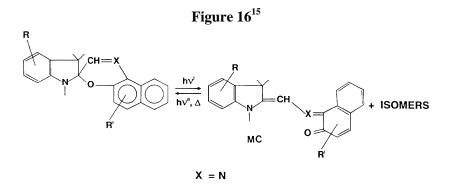
PHOTOCHROMIC COLORANTS:

There are various organic photochrome dye molecules, such as: triarylmethanes, stilbenes, azastilbenes, nitrones, fulgides, spiropyrans, naphtho pyrans and spiro-oxazines.

Almost all of these molecules have similar mechanisms of photochromism. As an example the oxazines mechanism will be explained.

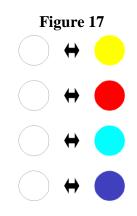
The colorless form of the oxazines contains a spiro carbon atom. This carbon atom is SP3 hybridized and serves to separate the molecule into two halves. Each half is comprised of benzenoid heterocyclics whose pi systems are orthogonal and are not conjugated across the spiroc arbon atom. Because the localized pi systems are separated by this SP3 hybridized carbon, all absorptions are in the UV part of the spectrum, not in the visible. Hence, the molecule appears colorless in its unactivated form.

Upon exposure to ultraviolet radiation (UV), the bond between the spiro and the oxygen of the oxazine ruptures, and the molecule undergoes a geometric rearrangement. In this new "ring opened" form, the pi systems are joined and conjugated along the entire molecule, which is virtually planar. This lowers the energy of the transition, and thus, the molecule absorbs at longer wavelengths, i.e., in the visible spectrum. For the blue photochromics, this absorption is around 610 nanometers. The absorption of red photons from white light leaves a remaining color that is blue. This is the same explanation for why the sky is blue.



On removal of the UV source, the molecule relaxes to its original geometric conformation -- the closed spiro form with the carbon oxygen bond reforming. The net observation is a return to the colorless state. This bond breaking and reforming process combines to form a cycle that goes from the closed colorless spiro form to the open colored merocyanine form and back. All these photochromic dyes, whether oxazine or naphthopyran, function in much the same way.¹⁶

Usually there are four basic colors available, which are a violet, a blue, a yellow and a red are schematically shown in Figure 16.



These colorants can be mixed like process colors to make some new colors such a by mixing a blue and a yellow to get a green, etc.



These colorants can easily be mixed in most common ink solvents, but sometimes it is better to use the "pigmentary" form that is manufactured by micro encapsulating the dyes in a carrier resin. The particle size distribution is usually between 1-6 microns, which lends itself to use with most printing systems if proper precautions are taken. Some of these colorants have excellent weather ability and light fastness, and some others have quite poor light and chemical fastnesses. It is best to discuss with the suppliers prior to using them

THERMOCHROMIC COLORANTS:

Thermochromic colorants can be both inorganic and organic. Amongst the inorganic chemicals that have thermochromism we can count Cobalt Chloride that changes from a faint pink to a blue at 35 $^{\circ}$ C and Nickel Sulfate which is green at room temperature but becomes yellow at 155 $^{\circ}$ C.

The thermochromic mechanisms of the organic molecules are different than the ones for inorganics. Most of these molecules can be custom manufactured to work in different temperature ranges. For example, one manufacturer offers nine different colors and temperature ranges from -15 °C to 70 °C.

The colors (approximations) are as shown in Figure 18:



These colorants are best used in either an emulsion form or in a quasi pigmentary form (microencapsulated) and again their particle sizes are between 1-6 microns, and can be used by most common printing methods: these range from screen inks for T-shirts or coffee mugs to offset litho for security applications. These dyes have are sensitive to light and some chemicals and it is advisable to discuss with the suppliers prior to using them

CONCLUSION:

All these colorants have unique characteristics that make them useful in printing inks. Some have been with us for a very long time, some others are quite recent innovations. Everyday there are new uses that are being created. Learn how to use them properly, innovate with them and you will advance the art of ink making and printing.

END NOTES:

¹ Becidyan, A. N., United Mineral & Chemical Corp., Lyndhurst, NJ, *Luminescent Pigments in Security Applications*, **COLOR research and application**, Vol. 20, Number 2, April 1995

² Private Correspondence with Streitel, Steven, Day Glo Corp., Cleveland, OH, (Copyright 1990-2001© Steven Streitel)

- ³ Copyright ©1995-1998 by Amethyst Galleries, Inc. from http://mineral.galleries.com/agi.htm
- ⁴ Fundamentals of Luminescence, Shionoya, S. and Yen, W.M., Editors, **Phosphor Handbook**, CRC Press, P. 61, 1998

⁵ Springsteen, Art W., PhD, Labsphere Inc., North Sutton, NH, *Fluorescence & Color*, a monograph published by Labsphere Inc., North Sutton, NH

⁶ Byler, William H., *Luminescent Pigments, Inorganic*, in **Handbook of Pigments**, John Wiley & Sons, I-I-b, 1977, pp.905-923

⁷ *LumiNova*[®] is a Registered Trademark of Nemoto & Co., Ltd. of Tokyo, Japan

⁸ OVP® is a Registered Trademark of Flex Products Inc., Santa Rosa, CA

⁹ Schmid, Raimund, et al, BASF AG, Ludwigshafen, Germany, from a paper presented at the 4th Nürnberg

Congress" (Nürnberg, 7-9 April, 1997), which was jointly organized by the Paint Research Association, Teddington, UK, and Vincentz Verlag, Hannover, Germany

¹⁰ Iden, Rüdiger, *et al*, BASF AG, Ludwigshafen, Germany *New Challenges in the Ways of Making Color*, **MODERN PAINTS AND COATINGS**, April 1999, pp 32-40.

¹¹ Parker, Barbara, Flex Products, Inc., Santa Rosa, CA, Using New High performance Color Shift Pigments to Create Dramatic Color Effects, from a paper presented at RETEC 1998.

¹² Iden, Rüdiger, et al, BASF AG, Ludwigshafen, Germany New Challenges in the Ways of Making Color, **MODERN PAINTS AND COATINGS**, April 1999, pp 32-40..

¹³ Bretler, Haim, SICPA S.A., Switzerland, *Thin Film devices in Security Printing Inks*, paper given at Conference on Optical Security, Los Angeles, CA, 1990

¹⁴ Figure courtesy of Flex Products Inc, Santa Rosa CA. Copyright 1995-2001© Flex Products Inc, Santa Rosa CA

¹⁵ Malatesta, V., Great Lakes Chemical Italia S.r.L, S. Donato, Italy, *Photochromic Dyes: How Long Do They Last?*, Paper given SPE Conference Effects in Plastics, 1993

¹⁶ PPG's Photosol® Photochromic Dyes, Copyright 1996-2001© PPG Industries, Inc. from http://www.ppg.com/_private/FrameResult.asp?f=/chm_optical/psol/default.htm

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