

# Physical Colors By Nanoparticle Resonant Color Pigments For High-Quality Printing Processes

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## Abstract

We are describing two methods of making physical colors. First we consider resonant excitation of high dielectric constant nanospheres (for example Si) coupled with absorption of the entrapped radiation. Alternatively we use absorption in metallic spheres, which exhibit negative real parts of the dielectric constant. Peak absorption occurs where the negative real part of the dielectric constant equals twice the positive dielectric constant of the surrounding medium. Absorption can be much larger than what could be achieved in conventional pigments leading to smaller required total volume of pigment.

## Introduction

To exceed the quality of photographic prints, including that of film transparencies, in digitally generated, non-impact prints or indeed any other printing method, one must begin with examining the properties of the inks which are used to construct the printed image. Two of the criteria for determining the suitability of an ink to attain the desired print quality, apart from process-induced artifacts, are:

1. The light stability and reproducibility of the pigment colorant;
2. The elimination of optical noise (gray content) innate to the ink so as to achieve clear, transparent colors.

To achieve these two objectives, while also sharply reducing the pigment concentration in the ink medium, a new direction for creating color effects was initiated whose central aim is to produce non-chemical colors.

We shall describe here new methods for achieving color by means other than using selective absorption through electronic transitions in atoms or molecules, such as dyes. The color will be produced by physical effects such as resonance of electromagnetic radiation in dielectric resonators of a size comparable to but smaller than a wavelength of light. A high index of refraction or equivalently a high dielectric constant is needed for high Q resonators leading to selective entrapment of radiation. The absorption wavelengths and thus color exhibited will

depend upon particle size. The effect can be looked at as an entrapment of resonance radiation inside the dielectric sphere followed by absorption. Even low intrinsic absorption in the dielectric will absorb all of the trapped radiation in a short time.

Alternatively color can be produced by the so-called Froehlich resonance, which is a totally different type of resonance. Here one uses the fact that for a number of metals and metallic compounds the real index of refraction can become negative in the visible spectrum. This in turn leads to a high absorption in the metal by a mechanism to be described below. Basically the electric field inside the metal sphere becomes very large for those wavelengths where the condition is satisfied that the negative value of the dielectric constant inside the sphere is equal in magnitude to twice the positive dielectric constant of the medium surrounding the sphere. When this condition is satisfied, then the electromagnetic fields inside the sphere become very large and subsequently metallic absorption leads to the extinction of those light wavelengths. The resonance condition and thereby the color can be moderately shifted by index changes in the carrier medium. The absorption wavelength is virtually independent of particle size. Both above described resonances can lead to absorption cross sections which are larger than one. This means that more light can be absorbed than falls onto the particles as described by geometric optics. We need to add that in any case geometric optics is not applicable for dimensions small compared to a wavelength of light. Nevertheless much less pigment is needed than with conventional colorants which are limited to absorption cross sections of unity.

## Color by Resonance Entrapment of Radiation in Nonmetallic Dielectric Spherical Resonators

It is well known from microwave technology that good cavities can be made from a high dielectric material alone, without any metallic walls. Radiation can be trapped by total or near total reflection from dielectric - air boundaries.<sup>1</sup> The lowest modes in a sphere are known as the  $TE_{1m1}$  and  $TM_{1m1}$  resonances. From perturbation theory one can calculate the approximate resonance wavelengths. For the  $TE_{1m1}$  mode one obtains

$$\lambda = \frac{2nr}{1 - \frac{1}{n^2 + jn\pi}}$$

Similarly the expression for the second lowest  $TM_{lm1}$  mode becomes

$$\lambda = \frac{2\pi nr}{x_0 - \frac{2\pi nr}{(n^3 + 2n - nx_0^2) + j(n^2 x_0 + 3x_0)}}$$

with  $x_0=4.4934$ .

In the above expressions  $\lambda$  is the vacuum wavelength for resonance,  $n$  is the index of refraction of the sphere,  $r$  is the sphere radius, and

$$j = \sqrt{-1}.$$

In the approximation of large  $n$  we can calculate the ratios of the wavelengths of the two lowest order modes

$$\frac{\lambda_{TE}}{\lambda_{TM}} = \frac{x_0}{\pi} \cong 1.43$$

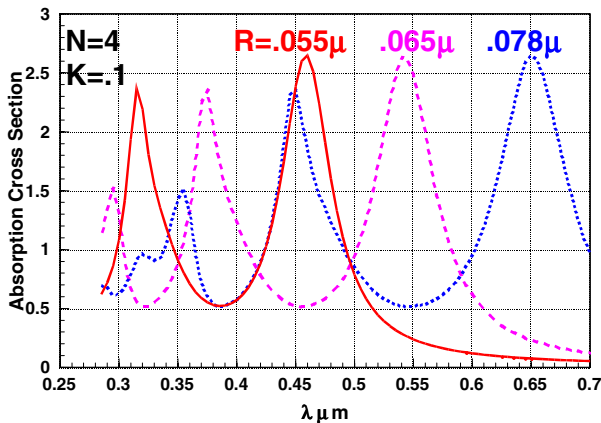


Figure 1. Absorption Cross Section of three spheres with radii 0.055 micron, .065 micron and .078 micron. The refractive index is 4 and its imaginary part is 0.1, values not far from those of Silicon. The visible spectrum is from 0.4 to 0.7 micron wavelength. The spheres with radii of 0.055 and 0.065 micron have only one absorption peak in the visible spectrum, while the sphere with a radius of 0.078 micron has two such absorption peaks (resonances).

Thus when the TM mode just enters the visible spectrum at 0.4 micron then the TE mode lies at 0.572 micron, which is near the transition from the green to the red portion of the spectrum. Thus if  $n$  is constant and independent upon wavelength then one can have only one absorption line anywhere in the spectrum between .4 and .572 micron. As the radius of the sphere becomes larger the  $TE_{lm1}$  moves further into the red and another mode

( $TM_{lm1}$ ) moves into the blue and we have two absorptions in the visible spectrum, one of which lies in the red somewhere beyond 0.572 micron. This is one of the limiting factors that has to be kept in mind when considering resonance colors, based on resonance entrapment: There are restrictions if one wants only one absorption line, especially if this line is near or in the red spectrum. We are illustrating this in Figure 1 through a detailed calculation using exact computer solutions of the Mie equations where we show the absorption cross sections of three spheres with different radii. The index of the material was chosen to be 4. The material has to be at least weakly absorbing or otherwise, even in the presence of resonances, there could not be any absorption. We thus choose a complex index of refraction with an imaginary part of 0.1. These index values are close to those of crystalline Silicon.

We shall see later that it is relatively more straightforward to have a red only absorption by the Froehlich resonance. Thus we need not excessively worry about red only absorption (blue color in transparency) through resonance spheres. In principle, we can make all colors by using both physical resonances, but in different materials.

### Metal Pigments Absorption By Froehlich Resonance

We shall consider here highly conductive metallic spheres. Metals have very different properties than pigments or resonant high dielectric constant spheres. The index of refraction usually has only a small real part indicating low or no trapping of radiation inside the sphere and any radiation trapped there would get absorbed very rapidly so that bulk resonance modes would hardly be expected. Nevertheless the recently observed blue color exhibited by metallic TiN spheres shows a new approach. In the long distant past colloidal gold particles were used to color ornamental glass windows with a deep red color. The observed TiN colors are based on similar physical principles. As we shall show similar colors are expected from ZrN, HfN and their alloys with TiN. Only limited experimental work has been done. The calculations below are expected to be exact, provided we can make spheres with the same optical constants of the materials as they have been measured on bulk pieces or on thin films. We give in the following a short general explanation of the effect. It should not be confused with resonance trapping of radiation by high dielectric constant spheres, such as silicon or  $TiO_2$ . Our computer program of the Mie theory can again be used to quantitatively predict the optical behavior.

The peculiar property which is here of central importance is the fact that in many metals the real part of the dielectric constant is negative for optical frequencies. Drude has explained the origin of this effect: Free conduction electrons in a high frequency electric field exhibit an oscillatory motion. For unbound electrons the electron motion is 180 degrees out of phase with the field. This phenomenon is well known in all driven resonators,

even simple mechanical ones. Visualize, for example, the motion of a tennis ball attached by a weak rubber band to a hand moving rapidly back and forth. When the hand is in its maximum positive excursion on an imagined x- axis the tennis ball would be at its maximum negative excursion on the same axis, and vice versa. The weakly bound or unbound electrons in a high frequency electric field act basically in the same way. Electronic polarization is therefore negative. Since in elementary electrostatics it is shown that the polarization is proportional to  $\epsilon - 1$ , it follows that  $\epsilon$  is then smaller than one and it may in fact even be negative. In tables of optical constants of metals one finds usually tabulated the real and imaginary parts of the index of refraction, N and K, as a function of wavelength. The dielectric constant is the square of the index of refraction, or

$$\epsilon_{real} + j\epsilon_{imag} = (N + jK)^2 = N^2 - K^2 + 2jNK$$

or

$$\begin{aligned} \epsilon_{real} &= N^2 - K^2 \\ \epsilon_{imag} &= 2NK \end{aligned}$$

and thus it may be seen that  $\epsilon_{real}$  is negative when K is larger than N. A look at the above-alluded tables reveals that indeed this condition is sometimes satisfied in the visible spectrum.

Also in electrostatics one usually finds in textbooks derivations for the magnitude of the electric field inside a dielectric sphere, which is immersed in a constant surrounding field. In cases where the wavelength is much larger than the sphere radius the metal sphere is surrounded by an electric field, which is approximately constant over the dimensions of the sphere, and thus the electrostatic approximations become appropriate for estimating the magnitude of the field inside of the sphere. From elementary electrostatics we obtain

$$E_{inside} = E_{outside} \frac{3\epsilon_{outside}}{2\epsilon_{outside} + \epsilon_{inside}}$$

where  $E_{outside}$  is the surrounding field,  $E_{inside}$  is the field inside the sphere and  $\epsilon_{inside}$  and  $\epsilon_{outside}$  are the (real) relative dielectric constants inside the sphere and in the surrounding medium, respectively. From the above equation it becomes immediately obvious that the field inside the sphere would become infinitely large if the condition

$$2\epsilon_{outside} + \epsilon_{inside} = 0$$

would be satisfied. Since the dielectric constants at light wavelengths are usually complex the field would become only large but not infinite. In case of an oscillating electric field that is a part of the light wave, that large field inside the metallic sphere would of course also result in a correspondingly large absorption by the metal.

Basically the just discussed field enhancement is the cause of strong absorption peaks produced in certain metal nanospheres. Taking into account the complex dielectric constant lets one can calculate the approximate absorption cross section  $Q_{abs}$ , provided that the imaginary part of the dielectric constant is small. Leaving out a few steps, one finds

$$Q_{abs} = 12x \frac{\epsilon_{medium} \epsilon_{imag}}{(\epsilon_{real} + 2\epsilon_{medium})^2 + \epsilon_{imag}^2}$$

In the above equation  $\epsilon_{medium}$  is the dielectric constant of the medium,  $\epsilon_{real}$  and  $\epsilon_{imag}$  are the real and imaginary parts of the dielectric constant of the metal sphere. The quantity x is given by

$$x = 2\pi r N_{medium} / \lambda$$

where r is the sphere radius and  $\lambda$  is the wavelength and  $N_{medium}$  is the index of refraction of the medium. Again when that part of the denominator that is in brackets becomes zero, a maximum absorption is expected. For large values of absorption with a distinct and clearly delineated absorption region  $\epsilon_{imag}$  should stay small. Obviously the maximum absorption wavelength shifts when the dielectric constant of the medium is changed. This would be a way of fine-tuning the color for a given metal.

Using the Mie theory we calculated exactly the absorption cross-sections for spheres with a radius of 0.02  $\mu m$  of TiN, ZrN and HfN as shown in Figure 2.

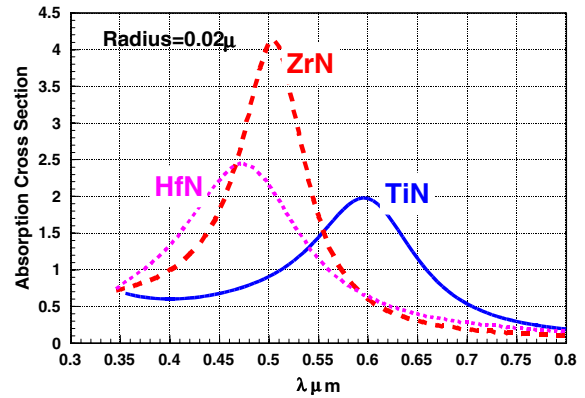


Figure 2. Absorption Cross Sections of TiN, ZrN, and HfN for a sphere radius of 0.02 micrometer.

In Figure 3 below we show the values of the real part of the dielectric constant that was used in obtaining the above shown absorption cross sections. The plot also illustrates the conditions and spectral locations of the Froehlich resonance. Gold spheres have absorption peak near 5200 Å. TiN, ZrN and HfN, which in bulk form look also golden colored, have peaks at shorter and longer wavelengths as shown above. TiN colloids have been

seen to exhibit a deep blue color because of absorption in the red and green spectrum.

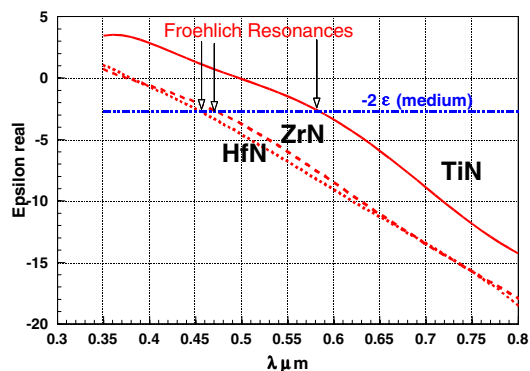


Figure 3. The real dielectric constant of three metallic Nitrides exhibiting a Fröhlich Resonance. The Fröhlich resonance frequency is determined by the position where the epsilon (real) curves intersect the line marked “-2 epsilon (medium)”

Again, in principle, we can make most colors by changing the metals through alloying and additions and by choosing different dielectric constants of the medium through corresponding material selections.

## Conclusions

Apart from using fundamentally different principles to generate permanent colors, the reader should notice that in the first case, nanoparticle color pigments must be selected and segregated by size (diameter of the spheres), whereas in the second type of physical color, the size does almost not matter; only the exact composition matters. Both approaches have advantages, some of them

relating to their mass production techniques. Because of the higher absorption cross sections ( $Q > 1$ ) volumetrically much less pigment is needed than with conventional approaches.

In any event, by creating this novel (patented) approach to generating permanent colors, we expect to visibly exceed the quality and gamut of photographic prints while enabling the use of advanced, digitally controllable printing techniques.

## References

1. R. E. Collins, Field Theory of Guided Waves, IEEE Press, Piscataway, NJ, 1991, p461.

## Biography

Dr. Manfred Kuehnle, Chairman of XMX Corporation, works closely with Dr. Statz on a number of breakthrough technologies emphasizing the fundamental importance of colorants in the form of nanoparticles and inks combined with novel, congruent area printing methods.

Hermann Statz holds a Dipl. Phys. and Dr. rer. nat. degree (1951) from the University of Stuttgart in Germany. He did postgraduate work from 1952 to 1953 with the Molecular and Solid State Theory Group at MIT. He then joined Raytheon where he retired as General Manager of the Research Division of Raytheon at the end of 1992. At Raytheon he worked on semiconductor technology, i.e. Silicon and especially GaAs as well as lasers and electro optic technologies. Since 1993 he worked with a number of organizations, including the XMX Corporation. Dr. Statz is a fellow of the American Physical Society and of the IEEE. He is also a Member of the National Academy of Engineering.