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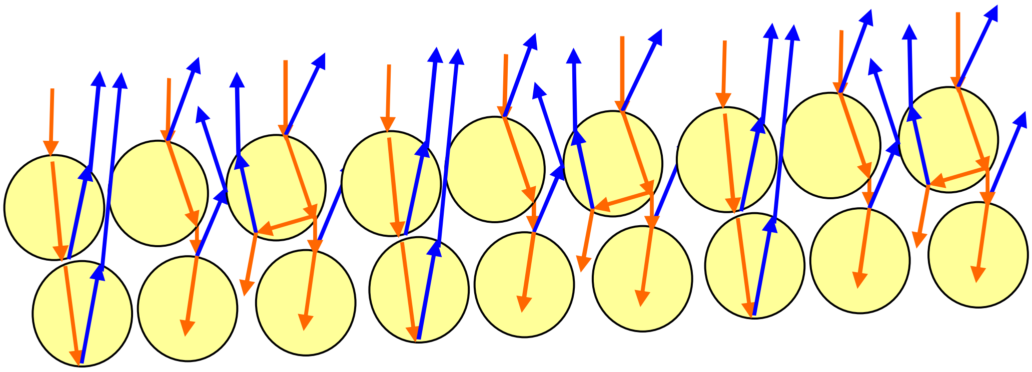
Technical report

Eva Hedborg Karlsson, Christina Nilsson, Tomas Hallberg, Hans Kariis

Pigments with Potential for Adaptable Optical Properties



Sensor Technology
SE-581 11 Linköping

SWEDISH DEFENCE RESEARCH AGENCY

Sensor Technology
P.O. Box 1165
SE-581 11 Linköping

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Author/s (editor/s)
Eva Hedborg Karlsson
Christina Nilsson
Tomas Hallberg
Hans Kariis

Project manager
Hans Kariis

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Abstract (not more than 200 words)

The main objective for the project, Pigments with Potential for Adaptable Optical Properties, is to produce material in which the electromagnetic properties can be controlled thereby enabling the object to adapt its signature to its background. This property is desirable within both the visible wavelength range as well as in the microwave and infrared ranges.

Paint consists of pigment and binders. For signature management applications, highly reflective paint in the infrared area of between 3-5 µm and 8-12 µm but low reflectance in the visible area, is usually desired. We have investigated how, through varying pigment particle composition and size, pigment can be designed with the desired reflectance properties. Particles of conducting (silver) as well as semi-conducting (silicon) and isolating (aluminum oxide) materials have been investigated. Particle sizes varied from 0,5 µm to 80 µm. The powders were studied in a scanning electron microscope and their reflectance measured in both the visible and infrared areas.

The results show that pigment material, particle size and shape of the particles are important for reflectance. The next step will be to produce paint by mixing pigment particles with a suitable binder. If this combination of pigment/binder is successful, we will be able to produce paint with potentially adaptable optical properties.

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Författare/redaktör
Eva Hedborg Karlsson
Christina Nilsson
Tomas Hallberg
Hans Kariis

Projektledare
Hans Kariis

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Pigment med potential för styrbarhet av optiska egenskaper

Sammanfattning (högst 200 ord)

Målet för projektet ”styrbara signaturmaterial” är att ta fram material vars elektromagnetiska egenskaper kan kontrolleras, så att objektets signatur kan anpassas till bakgrunden. Denna egenskap önskas i såväl det synliga våglängdsområdet som i mikrovågsområdet och infrarött.

Färg byggs upp av pigment och bindemedel. För signaturanpassningstillämpningar önskas vanligen färg med hög reflektans i IR-området (3-5 µm och 8-12 µm) men låg reflektans i det synliga området. Vi har undersökt hur man genom att variera sammansättningen och storleken på pigmentpartiklarna kan designa pigment med önskade reflektansegenskaper.

Partiklar av såväl ledande (silver) som halvledare (kisel) och isolerande (aluminiumoxid) material undersöktes. Partikelstorlekarna sträckte sig från 0,5 µm till 80 µm. Pulvren studerades i svepelektronmikroskop och deras reflektans mättes i det synliga våglängdsområdet och i IR-området.

Resultaten visar att pigmentmaterialet, partikelstorleken och partiklarnas form har betydelse för reflektansen. Nästa steg är att tillverka en färg genom att blanda pigmentpartiklar med lämpliga bindemedel. Om kombinationen pigment/bindemedel väljs på rätt sätt, kan vi framställa en färg med potential för styrbarhet.

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Innehållsförteckning

1 Introduction

The interaction of light with matter can result in one of three wave behaviours: absorption, reflection and transmission. Different objects have a tendency to selectively absorb, reflect or transmit light of certain frequencies, see Figure 1.

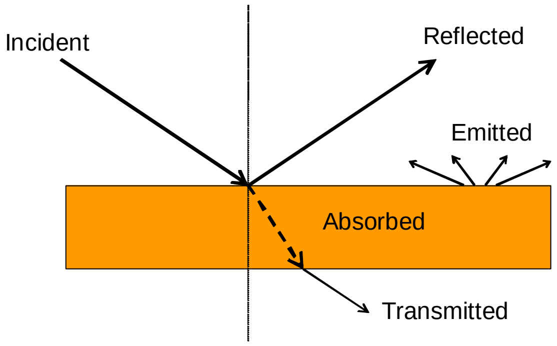


Figure 1. ***Absorption, transmission and reflection***

The electrons, atoms and molecules have specific allowed energy states. When a light wave with an energy that corresponds to the difference between two allowed states impinges upon atoms or molecules, the energy state might be changed into a higher excited state. This is true for radiation throughout the electromagnetic spectrum.

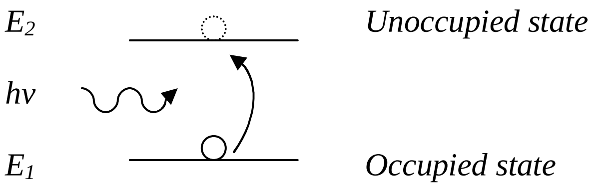


Figure 2. ***Excitation of electrons***

In the excited state, electrons (Figure 2) and atoms might interact with neighbouring atoms in such a atoms manner that the excited energy is converted into thermal energy. Consequently, the light wave is absorbed by the object, to be never released again in the form of light. So, the selective absorption of light by a particular material occurs because the frequency, hence its energy, of the light wave matches the difference in the energy levels of the electrons in the atoms. Since different atoms and molecules have different energies of excitation, they will selectively absorb different frequencies of light.

Reflection and transmission of light waves occur because the frequencies of the light waves do not match those frequencies of the object. If the object is transparent, then the energy of the electrons is passed on to neighbouring atoms through the bulk of the material and reemitted as a light wave on the opposite side of the object. If the object is opaque, then the energy is not passed from atom to atom through the bulk of the material. In this case the electrons vibrate for short periods of time and then reemit the energy as a reflected light wave. Such frequencies of light are reflected.

Reflection smooth surfaces leads to a type of reflection known as specular reflection. Reflection from rough surfaces leads to a type of reflection known as diffuse reflection see Figure 3.

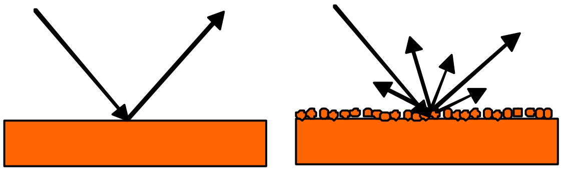


Figure 3. ***Specular and diffuse reflection***.

A cluster of many small particles, each of which reflects and/or transmits light, all together will scatter radiation in all directions. The particles/molecules that scatter light are called scatterers.

The scattering from molecules and very small particles (< 1/10 wavelength) is predominantly Rayleigh scattering. Rayleigh scattering can be considered to be elastic scattering since the photon energy of the scattered photons is not changed. For particles sizes larger than wavelength, Mie scattering dominates as shown in Figure 4.[1]

Scattering in which the energy is exchanged with the scattering objects is termed inelastic and is referred to as Raman scattering (Figure 5). In Raman scattering, the energy is shifted by an amount equal to the change in vibrational energy of the material through which the radiation is passing.

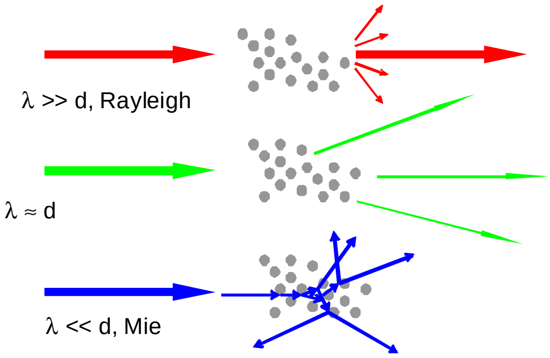


Figure 4. ***Rayleigh and Mie scattering***

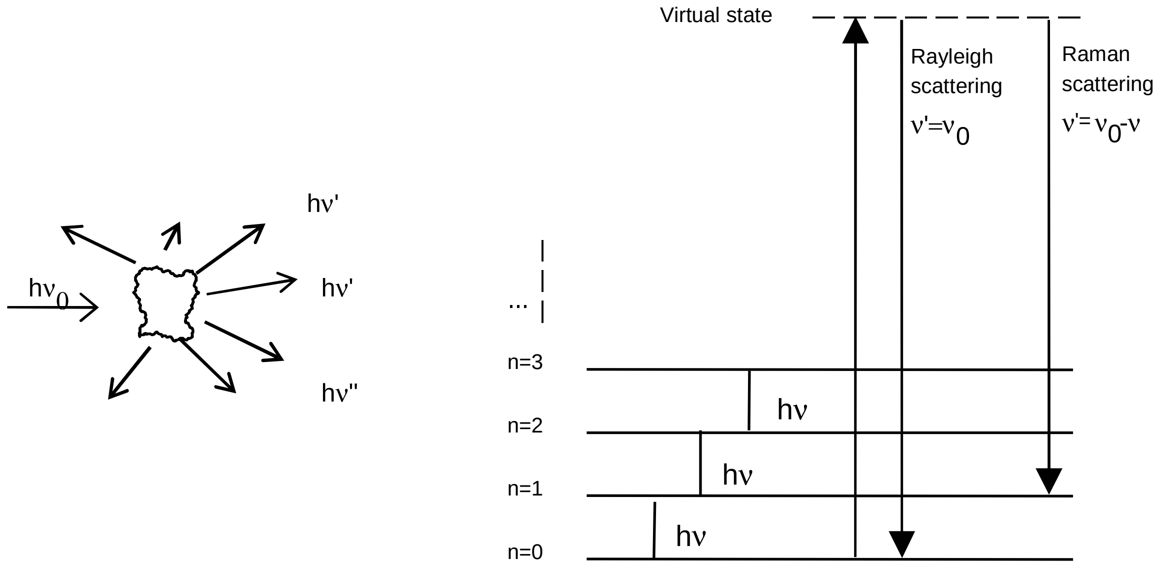


Figure 5. ***Raman scattering and Rayleigh scattering***

1.1 Reflecting and low infrared emitting coatings for defence use

Military objects have been camouflaged in a variety of different ways, which have the effect of making the object blend in with its background. For visual purposes, paints have been employed with a colour and finish to match the surroundings. It is also necessary to reduce infrared emission to a level where the camouflaged object has a similar emissivity to its background. For example, vegetation typically has an emissivity of about 0.5-0.6. The radiation bands of interest are apart from the visual, the near infrared NIR region between 0.7-2.5 µm, and the thermal infrared TIR region between 2.5-15 µm. In the far infrared region between 15-50 µm military sensors are rare.

The electromagnetic wavelengths which characterize NIR and TIR radiation permit the use of thin (a few microns) coatings to control absorption and reflection of radiation in these regions. The manner in which pigments and binders contribute to the spectral properties off a surface is important in formulating suitable coatings in desired spectral regions. Coatings can be designed to increase the reflection of incident radiation in the infrared region while retaining the visible properties of colour and gloss. The increased reflection reduces the apparent surface temperature and thereby lowers the energy requirements for cooling. In other instances, paints may be required to reduce the emission of thermal infrared radiation and shift infrared emission to other chosen wavelengths. For example the risk of detection can be reduced by only emitting radiation in the 5-8 µm region, where military sensors are not efficient due to the high atmospheric absorption. Coatings may also be formulated to combine reduced emission in the thermal region with reduced reflection in NIR bands used for laser detection. For windows in, for example, a cockpit it is desirable to transmit visible light while preventing the transmission of other infrared wavelengths.

The next generation of camouflage coatings requires new formulations that have controllable reflection, transmission, scattering and absorption/emissivity in a broad spectral region. To achieve this it is necessary to investigate which parameters are possible to control. How the emissivity is affected by the size distribution and physical shape of the pigment, and the choice of material must be investigated.

1.2 Control of optical properties

The colour of a coating is normally established for cosmetic or camouflage requirements. Camouflage of defence equipment in the visible waveband has traditionally been achieved by the use of dark coloured low gloss paints. These paints are commonly formulated with carbon black, which is a strong absorber of solar radiation and reduces visual and laser detectibility in the NIR. However, paint composed by carbon black[2] have high emissivity and therefore strongly emits thermal radiation. That means that surfaces coated with such paint are easy to detect in the TIR region.

A number of metal oxide coatings applied to metal substrates combine high visual and NIR absorption with low emissivity in the TIR, as thin oxide layers absorb short wavelength radiation but are transparent in the longer infrared region. These absorption characteristics act to reduce the chance of detection in the visual, NIR and TIR regions. However, heat build up may be a problem as the energy emission is prohibited. This problem could be addressed by allowing the energy to be emitted outside the atmospheric windows, e.g. 5-8 µm.

Highly conductive materials e.g. metals, do not allow electromagnetic propagation at optical or infrared frequencies. Paint with low thermal emissivity is usually formulated with metal pigments. Flaked metal pigments are commonly chosen because they have large flat surfaces, which maintain high reflectivity compared with smaller metal particles.

However, metals in the form of very small particles will allow the passage of decaying electromagnetic fields, and because of their high absorption, the emissivity of paints containing such particles is higher than that of a metal surface. These small particles will also provide diffuse multiple scattering, particularly when the particle size is close to the incident wavelength. This is the basis of the action for pigments called metallic blacks.

Scattering of visible and infrared radiation by a pigment is a function of the refractive indices of the pigment and the binder in which the pigment is dispersed. The refractive index of commercial pigments varies between 1.4 and 2.8. The scattering power of a pigment for white light is calculated by dividing the refractive index of the pigment by that of the binder. Pigments with scattering power well above 1 are called hiding pigments since they hide the substrate and modify the reflectance curve of the coating. Red iron and titanium dioxide are among the most effective hiding pigments, with values of 1.9. Extender pigments, for example silica, have values below 1.1; they scatter light poorly, do not alter the shape of the reflectance curve but do modify the reflectivity.

Common organic binders have refractive indices between 1.45 and 1.5 that means changes in scattering power cannot be achieved by the choice of conventional binder. For a fixed value of the scattering power *m* the wavelength most efficiently scattered by a particle of diameter *d* is given by Equation 1[3]

$$\lambda = \frac{d}{\kappa} \qquad (1)$$

in which

$$\kappa = \frac{0{,}9(m^2 + 2)}{n\pi(m^2 - 1)} \qquad (2)$$

In equation 2, n is the refractive index of the binder in the paint. To scatter thermal infrared radiation, particles of several micrometers in diameter would be required. Pigment that is transparent in the visible region but reflective in the infrared can increase the infrared reflectance without affecting the visible colour of the coating.

2 SEM and optical analysis of pigments

In this report we will describe the optical properties of pigments made from three different categories of materials (insulator, semiconductor and conductor), from the point of view of its physical morphology using spectroscopy and SEM. Measurements were made on pigments in the form of powder. These characterisations have been preformed on untreated pigment as well as on pigments heated to 200 °C in 5% H_2 in Ar for one and a half hour.

The size and the structure of the particles were characterized with a LEO 1550 FEG Scanning Electron Microscope (SEM). Their VIS and IR properties were characterized using a Varian Cary 5G for wavelengths 0.4 to 2 µm, and a Bruker IFS 55 for the wavelengths 1.6 to 25 µm. The diffuse reflection was collected by using integrating spheres with these spectrometers. The reflection values were calculated according to $R=(I/I_0)*R_0$ were I is the reflection signal from the sample, I_0 from a standard reflectance and R_0 the reflection of the reference.

2.1 Insulators

In a dielectric material the electrons are normally not elevated to the conducting band, except for very high energy photons, hence it is an insulator. Examples of such materials are silica and other oxides, as well as other solid ionic compounds. Many organic materials are also insulators such as polyethylene.

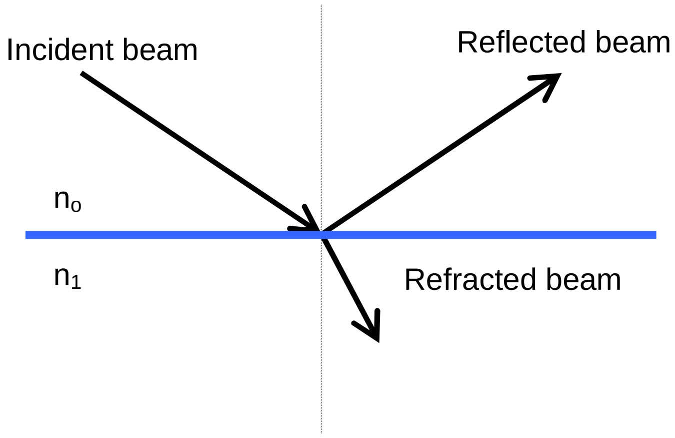


Figure 6. ***Electromagnetic wave crossing the border between two dielectric materials, n_1 with a higher refractive index than n_0.***

The electromagnetic field penetrates through the material with reduced velocity. The factor with which the velocity is reduced is called the refractive index of the material. At the interface between two dielectrics a part of the electromagnetic energy will be reflected, another part will be transmitted with a change in direction (refraction) see Figure 6. In materials with absorption the refractive index have en imaginary part not equal to zero.

In this work cenospheres exemplifies a dielectric pigment see Table 1. Cenospheres is a solid waste product obtained in large quantities during the burning of e.g. fossil fuel and coal. It consists of fine hollow spherical particles and the composition is somewhat variable, but the principal constituents are aluminum oxide and, silicon dioxide. The cenospheres were separated into different sizes by passing through sieves having different mask density.

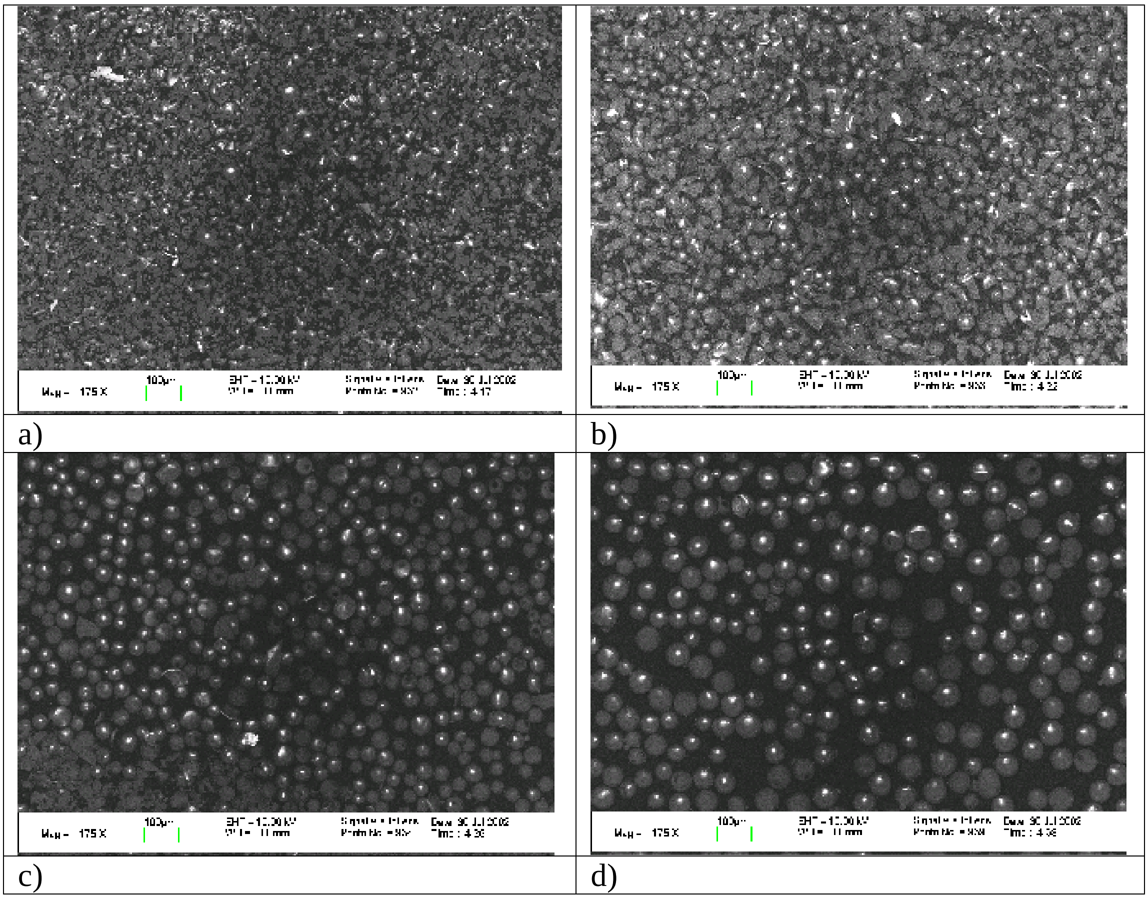
Measurements were done on four different size distributions, 20-36, 36-45, 45-63, and 63-80 µm.

Table 1: ***Investigated cenospheres***

Particle size [µm]	Supplier	Other comment
20-36	Trelleborg Fillite Limited	Partly crunshed
36-45	Trelleborg Fillite Limited	
45-63	Trelleborg Fillite Limited	
63-80	Trelleborg Fillite Limited	

2.1.1 SEM Analysis of Cenospheres

The particles were characterized with a scanning electron microscope (SEM).



a) b) c) d)

Figure 7. ***SEM pictures showing the size distributions of cenospheres: a) 20-36 µm, b) 36-45 µm, c) 45-63 µm, d) 63-80 µm***

The four images in Figure 7 show that the different sizes of the spheres are as expected, but the morphology varies considerably between the smaller and the bigger particles. Investigation of not sieved, different size, spheres in an ordinary microscope showed that all the particles were unbroken. This implies that the separation in the vibratory sieve shaker destroy the smaller cenospheres.

2.1.2 Reflectance Analysis of cenospheres

Visual spectroscopy

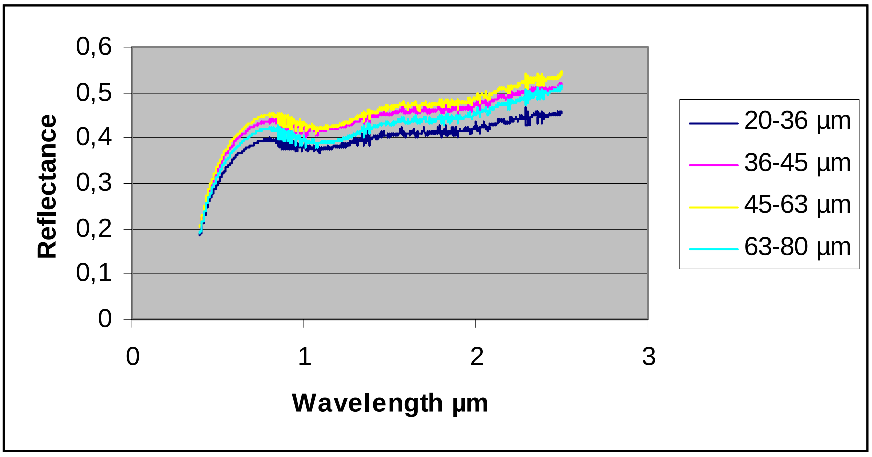


Figure 8. ***Measurements in the VIS and NIR region on different size distributions of cenosphere powder***

Figure 8 shows the reflectance, in the range 0.4-2.5 µm, of cenospheres with different size distributions. The spectra from cenospheres is very similar to that of quarts sand, with the reflectance increasing in the visual range and leveling in the NIR. The reflectance should in this case be enhanced by backscattering, in a similar manner which makes sugar and salt look white. Individual cenosphere particles are transparent and thus, light will be transmitted trough many layers of particles, where reflections will occur at each particle inteface. This backscattered reflectance will take place in the spectral range were the particles transmit. This is illustrated in Figure 9. The backscattering efficiency will increase if the difference between the refractive index of the particles and the ambient medium increases, which is the case for silicon powder presented in chapter 2.2.

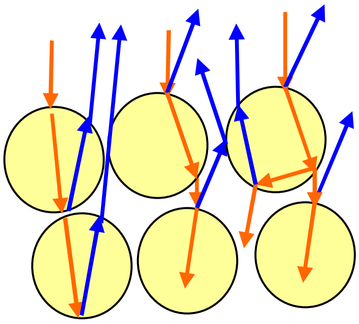


Figure 9 ***Principle for backscattered reflectance for transmitting particles.***

IR spectroscopy

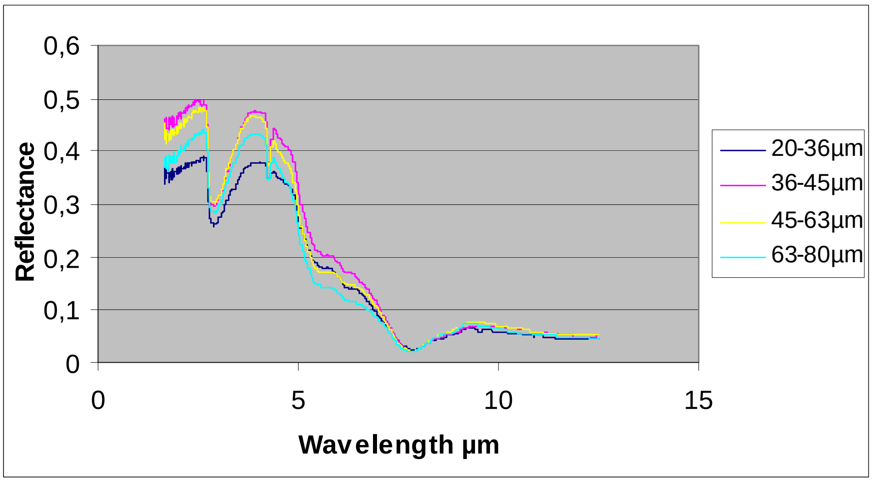


Figure 10. ***Measurement in the IR-region on different sizes cenospheres powder***

As can be seen in Figure 10 the reflectance was found to be rather low and almost the same for all the different size distributions of cenospheres in the region between 5-15 µm. The reason for the broad absorption bands in the thermal infrared region can be explained, since the cenospheres mainly consist of silicon dioxide (SiO_2) and aluminium oxide (Al_2O_3). Both of these oxides give rise to strong absorption in this region, which will reduce the backscattered reflectance mentioned above. In the region between 2-5 µm the reflectance level is different for different particle sizes. Particle size distributions between 36 µm and 63 µm have the highest reflectance values. The peak at 3-3.5 µm derives from O-H groups on the oxides. The small peak at about 4 µm is due to atmospheric CO_2 in the sample chamber.

2.2 Semiconductors

The electrons in semiconductors are normally bound, like in insulators. By adding a limited amount of energy, electrons can be transferred to the conduction band, giving the material conductive properties. For photon energies higher than the bandgap, a semiconductor is opaque. The bandgap of silicon corresponds to 1.1 µm in the NIR, thus wavelengths longer than this will be transmitted. However, semiconductors usually have very high refractive indices, hence their refractive power is high and they are therefore strong candidates as efficient IR-pigments. In this work Silicon exemplifies a semiconductor.

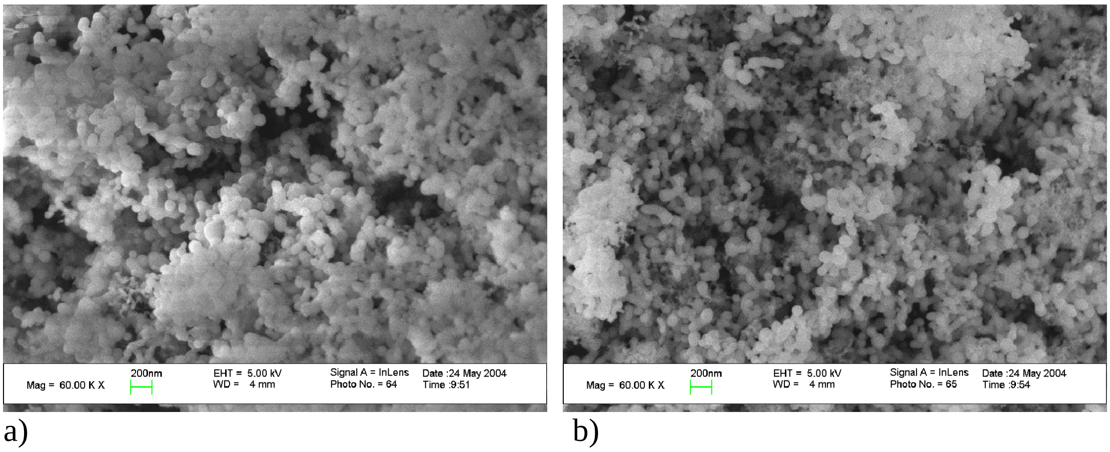
Table 2 *Investigated silicon powders*.

Particle size [µm]	Supplier	Other comment	Purity
0.07-0.10	Alfa Aesar	Crystalline	98%
1-2	Alfa Aesar	Nodular	99.999%
<50	Good Fellow		99.998%
50	Aldrich		99% (-325 mesh)
150	Alfa Aesar	crystaline	99,9% (-100 mesh)

Measurements were carried out on five different kinds of silicon powder, from different suppliers, shown in Table 2.

2.2.1 SEM Analysis of silicon

Figure 11 shows plane view SEM images of silicon pigments, with the size distributions a) 0.07-0.1 µm, b) 0,07-0.1 µm after heating in air. There are no observable difference between the pigments before and after the heat treatment.



a) b)

Figure 11. ***SEM plan view images of a) untreated 0.07-0.1 µm Si pigments b) 0.07-0.1 µm Si pigments after heat treatment at 200°C***

The pigments in Figure 12 are supposed to have the same size distribution. The SEM pictures clearly show that the physical shape of the pigments is quite different.

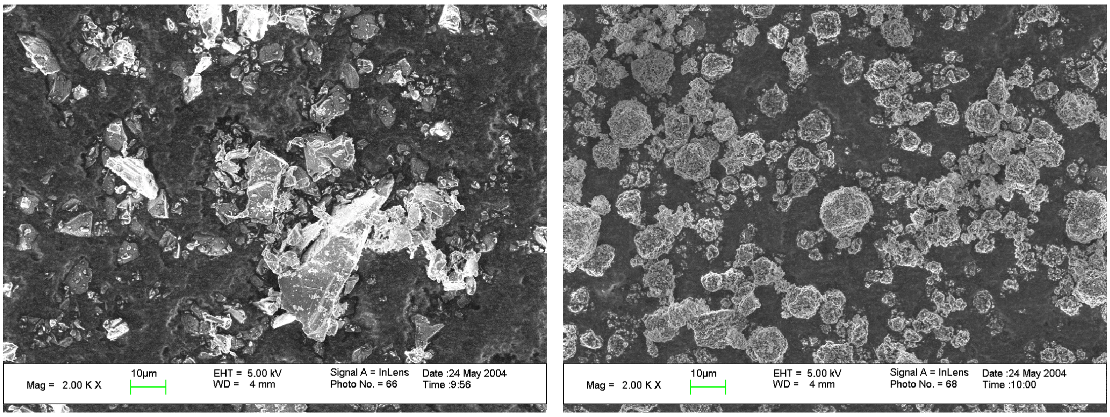


Figure 12. SEM plan view images of a) 50 µm Si pigments from Aldrich b) 50 µm Si pigments from Good Fellow

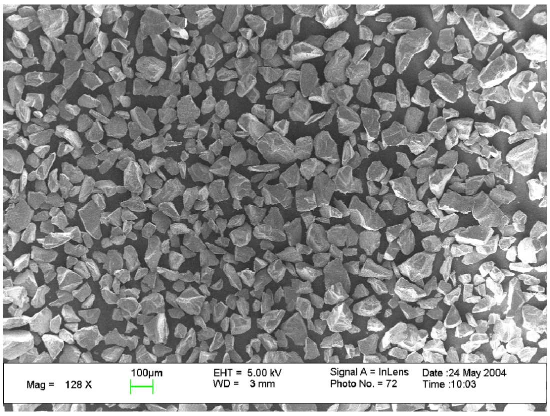


Figure 13. SEM plan view images of a) 150 µm Si pigments from Alfa Aesar

2.2.2 Reflectance analysis of silicon

Visual spectroscopy

Figure 14 shows the results of reflectance measurements in the wavelength range 0.4-2 µm on silicon particles of different size distributions.

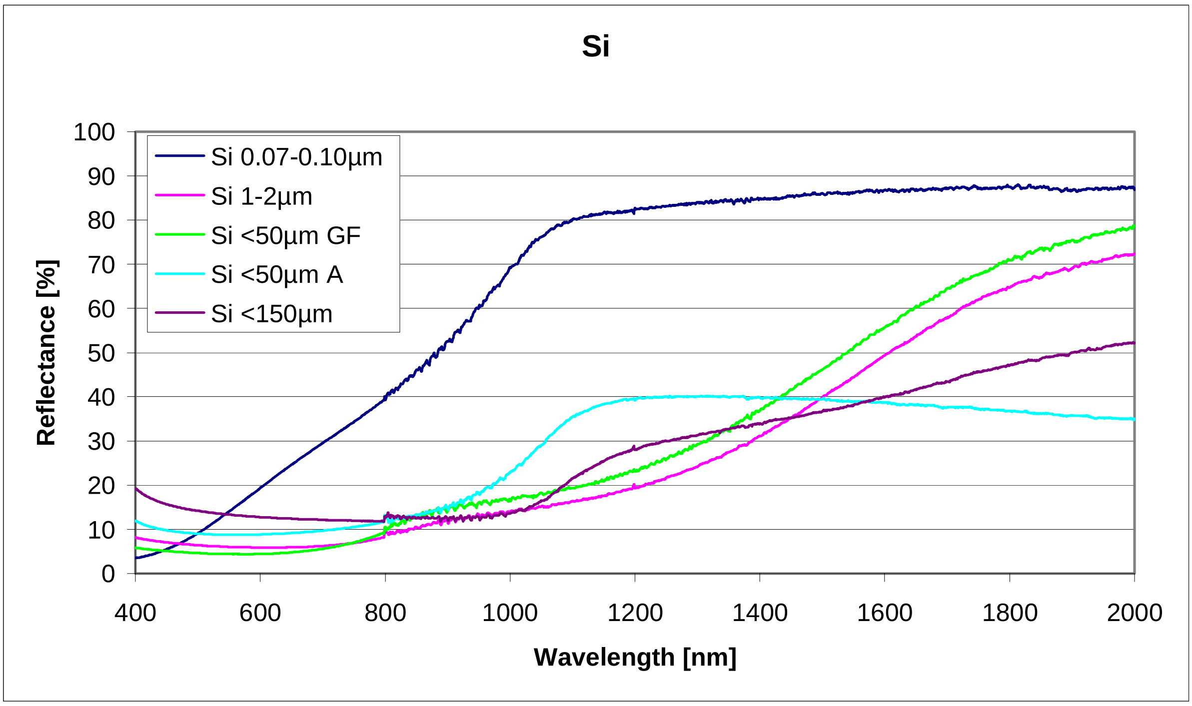


Figure 14. ***Reflectance for silicon particles of different size distributions in the visual and NIR range.***

The smallest particles (0.07-0.10 µm) show a low reflectance in the visual domain that steadily increases as it approaches the NIR region where it levels at a rather high reflectance close to 90%. The 1-2 µm and 50 µm (GF) size distributions show approximately the same wavelength dependence of the reflectance, only the larger size has a higher over all reflectance. On the other hand, the size distribution of two of the samples is very similar, 50 µm (GF) and 50 µm (A). However, the reflectances of these samples differ remarkably. This difference can be explained by the different form/structure of the pigments, compare with the SEM results in Figure 11.

IR spectroscopy

Measurements were performed on the different Si powder samples in the 1.6-25 µm range using an integrating sphere. The results are presented in Figure 15. The high reflectance of small silicon particles is due to back scattering of light, which is efficient in the part of the IR region where silicon transmits well and absorption is low. The main absorption features normally present in pure crystalline silicon is caused by phonons, i.e. collective vibrational modes of Si lattice atoms, and localized vibrational modes interstitially positioned oxygen (O_i). Phonon bands are present in the region 6.8-17.6 µm, with the main peaks positioned at about 11.1 µm, 13.4 µm and 16.3 µm (strongest). These bands are present in most of the spectra in Figure 15 O_i gives rise to a strong band at 9.0 µm and a weaker at 19.4 µm. However, these bands are in this case absent or hidden by bands related to SiO and SiO_2, with strong bands at 8-10 µm and weaker bands at 11.5-12.5 µm and 22-25 µm. The dominating SiO band is positioned at about 10 µm while these related to SiO_2 are in the 8-9 µm region.

A native SiO coating of about 30 Å is naturally occurring on a Si surface. This will grow in thickness upon heating in oxygen ambient. SiO will transform to SiO_2 upon heating above temperatures where the oxygen atom is mobile and is able to diffuse, i.e. above ca 350 °C. As x in SiO_x increases from 1 to 2, the band at 10 µm will gradually shift towards shorter wavelengths. The SiO_x may also appear in the bulk of Si as a defect formed by heating, due to the precipitation of O_i atoms.

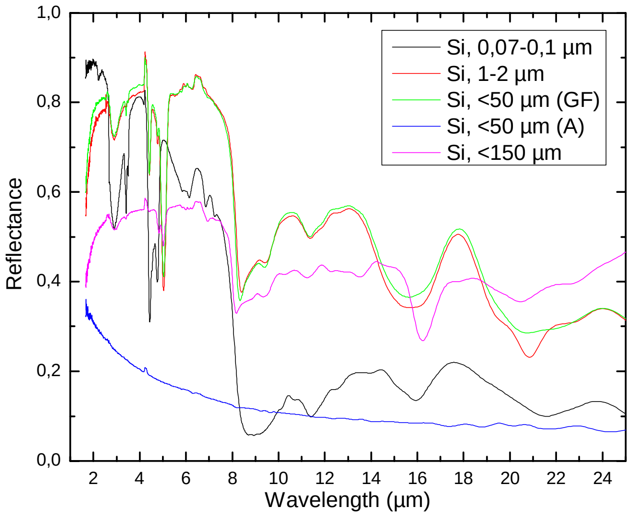


Figure 15. ***Spectra of silicon powder with different particle sizes***

In the region 1.1-9 µm there is normally no significant absorption present in silicon. In this case intense bands are present at about 3-3.5 µm and 4.5-5 µm. The broad band at about 3 µm is related to Si-OH, while two sharper bands at 3.4 and 3.5 µm are probably related to N or CH complexes. The bands in the 4.5-5 µm region are caused by Si-H vibrations. These complexes also have several other weaker bands in the 6-14 µm region.

From these observations we may assume that the silicon particles have been exposed to heat in a wet atmosphere. Also, organic complexes due to dirt may be present.

A particle size dependence is present as well in the spectra. The smallest sized particles have a stronger reflectance as compared to larger particles for shorter wavelengths, while the opposite appears to hold for longer wavelengths. There also seems to be a surface structure dependence. The Aldrich 50 µm powder deviates from the rest according to the SEM pictures showing a more irregular structure. From Figure 15 it seems like this gives rise to a comparatively low reflectance, probably because it affects the back scattering efficiency.

2.3 Conductors

Metals have free valence electrons. The electron cloud reflects an incoming electromagnetic wave with a frequency below the plasma frequency of the metal, which usually is in the ultraviolet region.

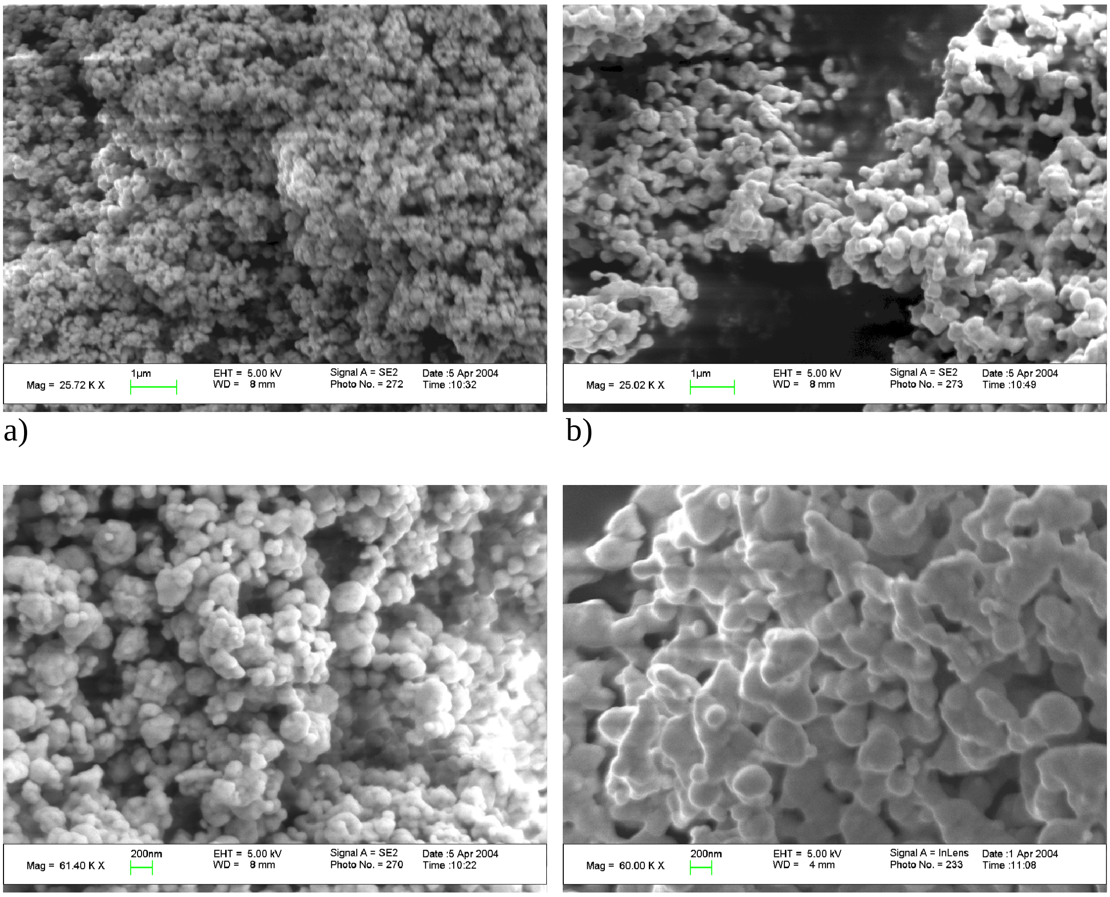
Table 3. ***Investigated silver powders.***

Particle size [µm]	Supplier	Other comment	Purity
0.5-1	Alfa Aesar		99.9%
<20	-		-
>20	-		-

Measurements were carried out on untreated and heated silver particles of three different sizes listed in Table 3.

2.3.1 SEM Analysis of silver

Figure 16 shows plan view SEM images of silver pigments. Analyses on three different size distributions have been carried out. From the SEM picture, Figure 16, it can be observed that silver pigments with the size distribution 0.5-1 µm agglomerates during the heating probably due to sintering. Sintering occurs in a controlled-atmosphere furnace where the pieces or powders are heated to a temperature close to but not at melting. This is done so that particles may bond by solid state bonding, but not melt. One factor that influences the sintering reactivity is surface oxidation. Most metal powders will oxidize to some extent when they are exposed to air. The surface oxide layer that is formed this way inhibits sintering. The particle size is very important for sintering reactivity; finer powders have a higher sintering reactivity than courser powders.



a) b)

c) d)

Figure 16. *SEM images of silver pigments with the size distribution 0,5-1 µm. a and c show images of untreated pigments at different magnification. In picture b and d the silver pigments are heat treated at 200 °C in 5%* H_2 *in Ar for one and a half hour*

In Figure 17 and Figure 18 it can be observed that silver pigments, with the larger size distribution, have similar physical appearance before and after the heat treatment.

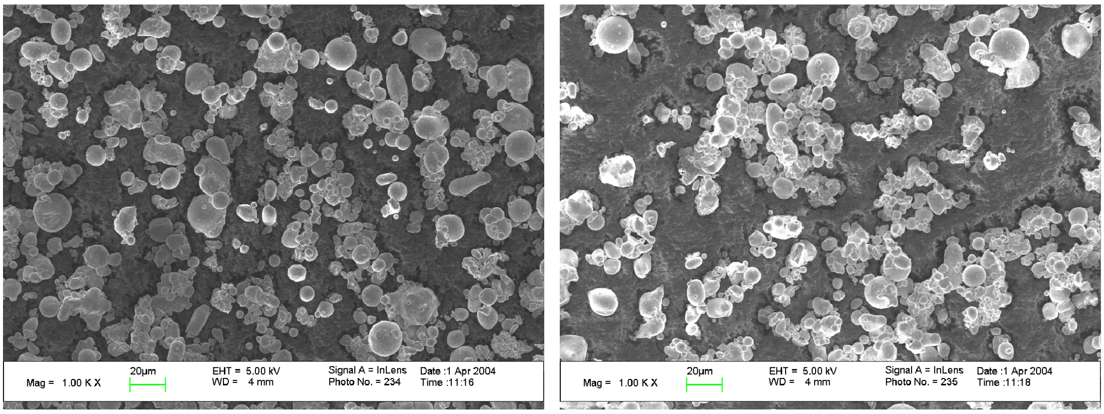


Figure 17. *SEM images of silver pigments with the size distribution < 20 µm. a) show untreated pigments. In picture b) the silver pigments are heat treated at 200 °C in 5%* H_2 *in Ar for one and a half hour.*

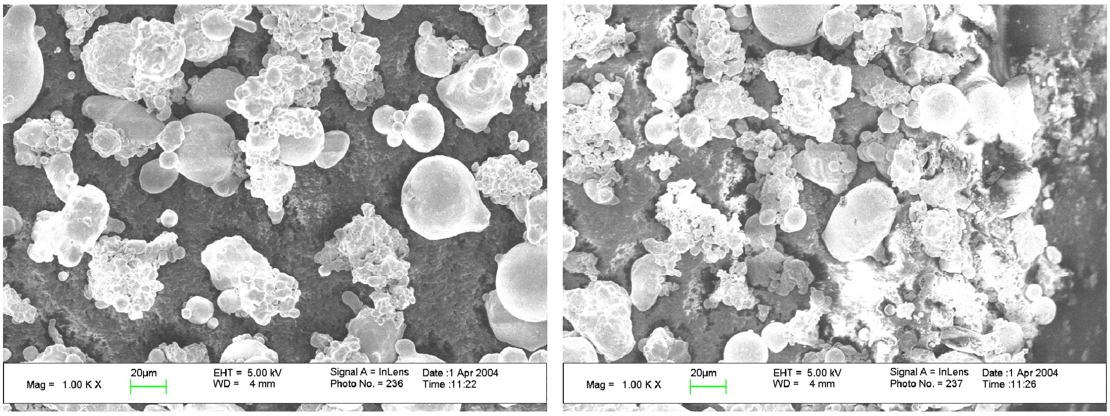


Figure 18. *SEM images of silver pigments with the size distribution > 20 µm. a show untreated pigments. In picture b the silver pigments are heat treated at 200 °C in 5% H_2 in Ar for one and a half hour.*

2.3.2 Reflectance analysis of silver

Visual spectroscopy

For all sizes the heated samples show higher reflectance than in the untreated case. The reason for this is that by heating the sample it is purified, whereby it receives higher reflectance. In the sample with particles >20 µm though, the difference between the untreated and heated is very small. On the other hand, the reflectance increases with the size of the powder/particles, due to the increased flatness of the surface.

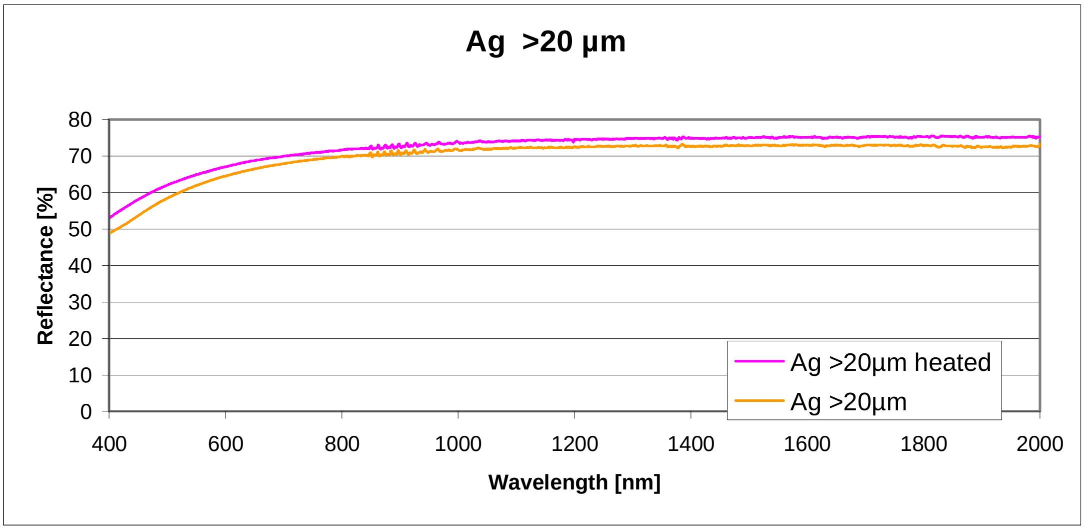


Figure 19. ***Reflectance for silver particles (> 20 µm) in the visual and NIR range***

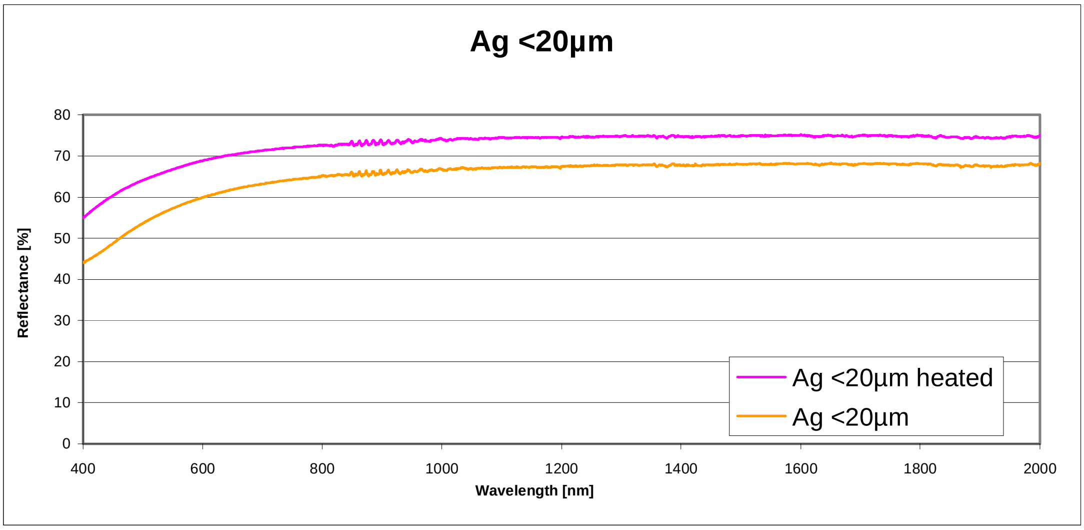


Figure 20. ***Reflectance for silver particles (< 20 µm) in the visual and NIR range***

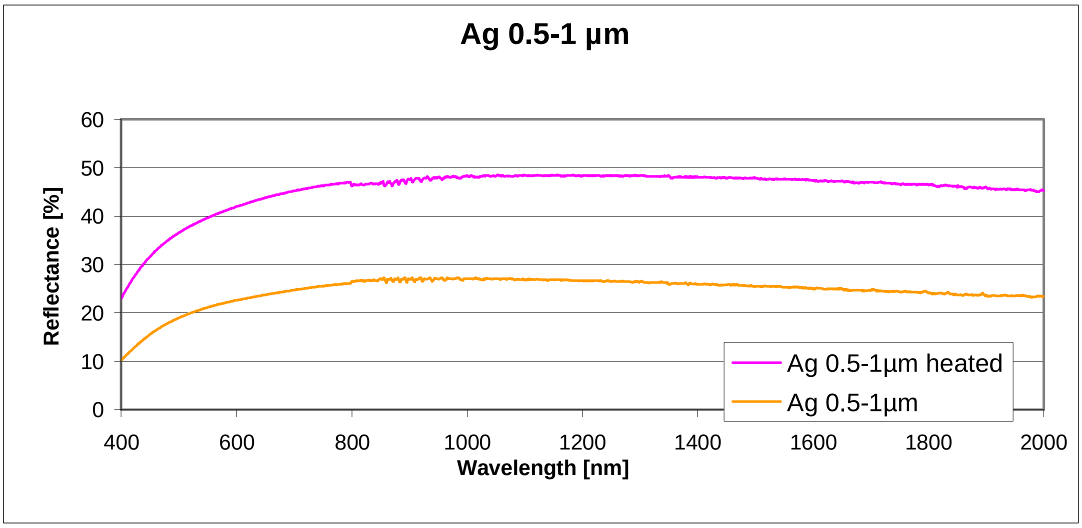


Figure 21 ***Reflectance for silver particles (0.5-1 µm) in the visual and NIR range.***

IR spectroscopy

Reflectance spectra of untreated and heated Ag powder of different sizes (

Table 3) are shown in Figure 22, Figure 23 and Figure 24. According to these figures, in untreated powder vibrational bands can be found in the regions 3.3-3.5 µm and 6.5-7.5 µm and around 9 µm. A band related to atmospheric CO_2 in the sample chamber is positioned at 4.2 µm. The origin of these bands should be from organic compounds like CH complexes. As expected these disappear during heat treatment, as in the figures.

The spectra in Figure 19-22 show a clear powder size dependence on the reflectance level. A small sized powder has a lower reflectance as compared to larger particles.

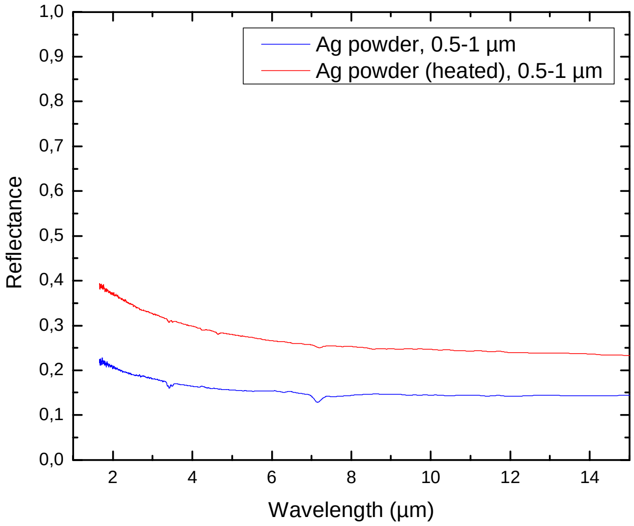


Figure 22. ***Reflectance of untreated and heated Ag powder with size distribution 0.5-1 µm***

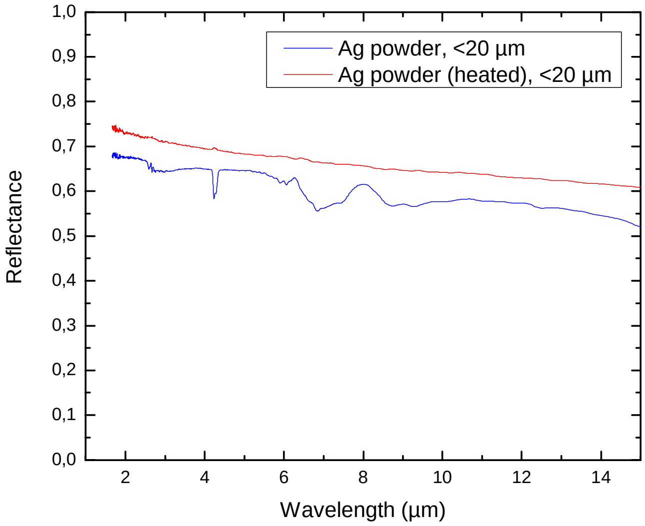


Figure 23. ***Reflectance of untreated and heated Ag powder with size distribution <20 µm***

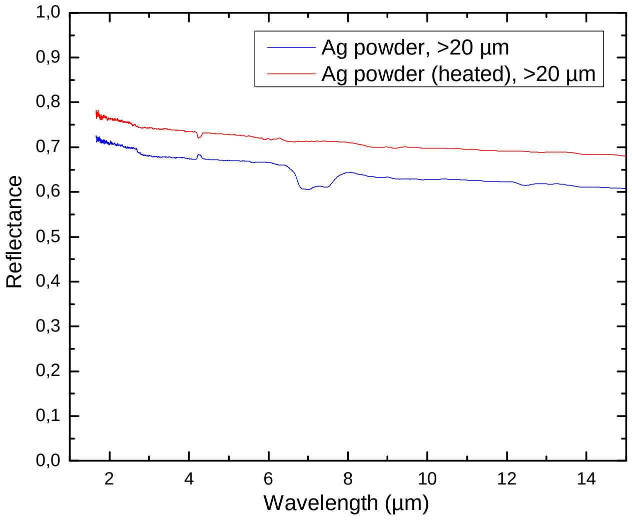


Figure 24. ***Reflectance of untreated and heated Ag powder with size distribution >20 µm***

3 Conclusions

The reflectance properties in the visual and IR have been analyzed for different pigments concerning the size distribution, the physical shape as well as material compositions. As a consequence we have increased our knowledge in this field, in order to be able to choose the right kind of pigment for each particular application.

Cenospheres show a fairly high reflectance up to 5 µm, but in TIR their reflectance is very low, due to absorption from oxides. However, this disadvantages can be dealt with by coating the cenospheres with a metallic layer to improve the reflectance. Some experiments have already been done on this [4]. Their low weight is an advantage for air and space applications. Another advantage is their well specified spherical shape, which makes them ideal as model pigment.

The high reflectance from both cenospheres and silicon is due to backscattering, since they both transmit in various wavelength ranges, and their reflectance is limited, because they absorb due to the presence of oxides. The maximum reflection is particle size dependent. Our results for cenospheres and silicon indicate that, small particle give rise to high reflectance at short wavelengths, while larger particles cause high reflectance at longer wavelengths. An exception is the smallest cenospheres, which were crunshed during the separation and therefore have another shape. They can on the other hand be compared with the silicon pigment of size <50 µm from Aldrich, that have a irregular shape with gives a lower reflectance. Seemingly an irregular shape gives rise to lower reflectance.

The absorption features in silicon due to various defects could be avoided by more careful production process or by heating, in order to remove impurities. It might be more difficult to completely reduce the oxide band in silicon. However, it might be possible, by dispersion at high temperatures to reduce or modify these oxides. Heat treatment of silicon particles to remove impurities should be performed in a similar way as was done on silver particles.

For metals the reflectance is lower the smaller the particles. This is contrary to the results for semiconductors and insulators. For bulk metals there is no transmission, only reflectance within the investigated ranges. For insulators and semiconductors, the light can be partly transmitted, and reflected on more surfaces. For metal particles, however, turns out to be more like a smooth flat surface as the particles becomes larger, whereby the reflectance increases. It is well know that a metal layers thin enough (<100 nm) can have some transmission. For small particles, there might be some transmission. Also, the absorption is probably higher among the small particles, because of the larger surface area.

Three factors influence the reflectance properties of a pigment; particle size, physical shape, and material composition. This knowledge gives us the opportunity to design a pigment that gives desired reflectance properties. One obvious application for these pigments is paint for signature management where high reflectance in the infra red combined with low reflectance in the visual is desired. Another application is paintable displays.

4 Future work

It is wished that future work includes a greater variation of particles, sizes and physical shape, to achieve greater knowledge of optical properties and context of everything. It would also be interesting to study the influence of coating of different thicknesses on (cenospheres) particles of different sizes and of different materials. Are there any thicknesses where the reflectance is independent of the particle size? For which coating thickness does the metal coating properties dominate over the substrate properties? Further, a greater exchange with theoretical modeling on the impact of physical shape on the reflectance is important.

It is possible to control the reflectance by using thermo- or electrochromic pigments, which change reflectance when the temperature or the voltage is changed. Another possibility is to control the optical properties of the binder by using for instance conducting polymers. Furthermore electrophoreses of pigment particle can be used to control reflectance properties of pigment in a similar way as to electronic ink. In the near future this will be studied.

Earlier pigment studies have been made to accomplish a low emissive paint. The pigment has then been mixed with a binder. Some work has already been done in this field[5], *i.e.* to understand how a binder contributes to the total/overall reflectance as well as how pigment and a binder interacts on a surface. More effort must be put in to this field though.

Most of organic resins or binders are free from strong absorption in the visible and the NIR region and can be used for many applications in this part of the spectrum. However, in the TIR region, organic resin/binders show strong absorption bands due to molecular vibrations of their functional groups; bands near 3,3 (C-H stretch), 5,7 (C-O stretch), 7.0 (C-H bending) and 8,0 (C-O stretch) are usually prominent.

In the future we will try to avoid this problem by choosing binders which do not contain common functional groups. Poly(vinylidene fluoride) resins are almost transparent to and unaffected by solar radiation, and have only weak absorption in the TIR region[6]. They have excellent weather stability and show great promise for tailored infrared coatings. Dimethyl silicone resins have emittance values lower than those of fully organic resins and have been used for low emittance coatings[7]. Inorganic silicate oligomers form polymers which contain only silicon-oxygen bonds[8], these resins show low emittance exept for a band near 9 µm.

Combined with appropriate binder these pigments have potential for design of adaptable materials. Such material combinations will be further studied within the project.

5 References

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