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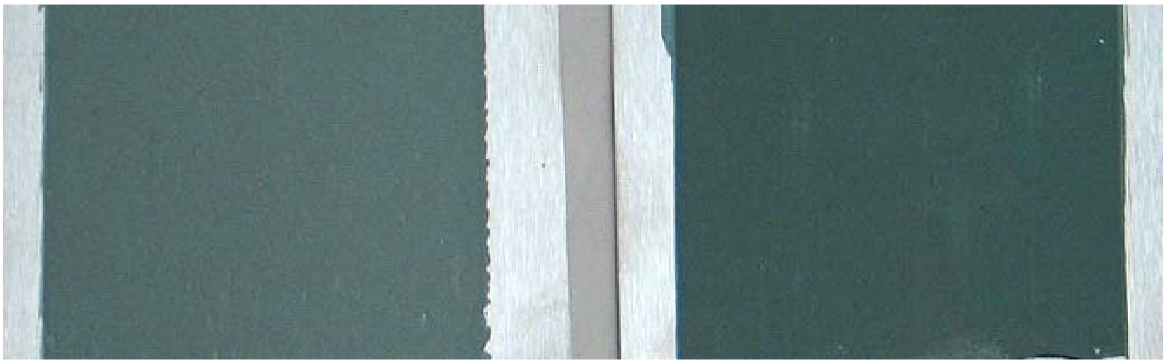
Development of low-emissive camouflage paint:

Final report



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Report title

Development of low-emissive camouflage paint: Final report

Abstract (not more than 200 words)

This report concludes a collaboration project between the Swedish Defence Research Agency and the Finnish Defence Forces Technical Research Centre, on the development of low-emissive paint for camouflage in the IR, without loosing performance in the visual region. Different types of pigments and polymer based binders have been tested, both individually and mixed together as paint, also including various additives. IR-reflecting pigments such as Al, Ag, Cu, coated metal pigments, metal coated cenospheres, Si and multiple-layers of TiO_2/Au/TiO_2 were used in the shapes of flakes or spherical particles of different size distributions. Coated metal pigments and multiple-layer flakes were used in order to decrease the reflectance in the visual range. One conclusion is that among these pigments only aluminium-based paint gave rise to acceptably low emissivity. Various pigmentation colours were used for visual effect. Radar transmission properties of paint were also investigated.

Keywords

low-emissive, paint, binder, pigment

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Framtagning av en lågemissiv maskeringsfärg: Slutrapport

Sammanfattning (högst 200 ord)

Den här rapporten sammanfattar ett projektsamarbete mellan FOI och Finska PvTT (Finnish Defence Forces Technical Research Centre) rörande framställning av lågemissiv färg för maskering i det infraröda våglängdsområdet, utan att förlora önskade visuella färgegenskaper. Olika typer av pigment och polymerbaserade bindemedel har testats, både individuellt och blandat till färg, även innehållande olika tillsatsmedel. IR-reflekterande pigment såsom Al, Ag, Cu, belagda metallpigment, metallbelagda cenosfärer, Si och multilager av TiO_2/Au/TiO_2 användes i form av flingor eller sfäriska partiklar i olika storlekar. Belagda metallpigment och flingor av multilager användes för att sänka reflektansen i det visuella området. En slutsats är att bland dessa pigment ger endast färg baserad på aluminiumpartiklar acceptabelt låg emissivitet. Olika färgpigment användes för visuell effekt. Radartransmissionsegenskaper hos färg undersöktes också.

Nyckelord

lågemissiv, färg, bindemedel, pigment

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Contents

Introduction

Due to the development of IR detectors during the last couple of decades for the use in, e.g., missile seekers, surveillance systems and search and track systems, the thermal signature of military targets normally has to be reduced in order to avoid detection against the background. The development of such sensors continues towards systems with still higher performance, concerning detectivity, resolution (spatial, spectral, temporal) and spectral sensitivity in several wavelength bands. Also, considerable effort is focused on developing advanced signal processing in order to allow detection, identification and classification even at a low signal to noise ratio. There are several possible methods by which the thermal signature could be reduced, e.g., for a ground vehicle, like insulation around the engine compartment, air or water cooling pipes underneath the body or heat reflecting coatings on top of the vehicle body. This paper concerns the development of a low-emissive paint.

The collaboration between the Finnish Defence Forces Technical Research Centre (PvTT) and the Swedish Defence Research Agency (FOI) on the development of a low-emissive paint, for camouflage in the IR and visual wavelength regions, started in year 2000. The collaboration was motivated by the facts that PvTT had previous experience in developing various winter and summer camouflage paints [1] and that FOI was working with different pigments [2-6] and binders [7] for camouflage paint with low IR emissive properties. The collaboration project (CP) has been in accordance with a Memorandum of Understanding between the defence research agencies in Denmark, Finland, Norway, and Sweden.

The aim of the collaboration was to find a combination of pigments, binders and additives, i.e. a paint, which would give high camouflage efficiency both in the IR and the visual regions. In order to fulfil this goal, different pigments and binders were characterized, both individually and mixed together as paint. Pigments commercially available, as well as such developed by FOI and PvTT, have been used. The paint should also undergo different trials in order to determine the effects of weather, how cleaning will affect the IR and visual reflectance properties and mechanical and physical properties of coatings. However, these trials were not performed within this collaboration. On the other hand, the radar transmission properties of the paint have been characterized, though this was not included as an objective within the CP. It is important to maximise the radar transmission through paint in case it should be applied on a radar absorbing material (RAM).

Emissivity and highly reflective pigments

The reflectance (ρ) and emissivity (ε) are important parameters in this context. The emissivity is defined as the ratio of the radiance from a surface sample (L_s) at a given temperature T and wavelength λ, to that of a blackbody radiator (L_{BB}) at the same temperature and wavelength. Thus, ε is expressed as

$$\varepsilon(\lambda,T) = \frac{L_s(\lambda,T)}{L_{BB}(\lambda,T)}\,. \tag{1}$$

Radiation from the surroundings reflected into the sample and the reference surface has to be considered when making measurements. ρ and ε are related to each other according to the Kirchhoff’s law, which in case the transmission through the sample is zero, is given as

$$\rho = 1 - \varepsilon\,. \tag{2}$$

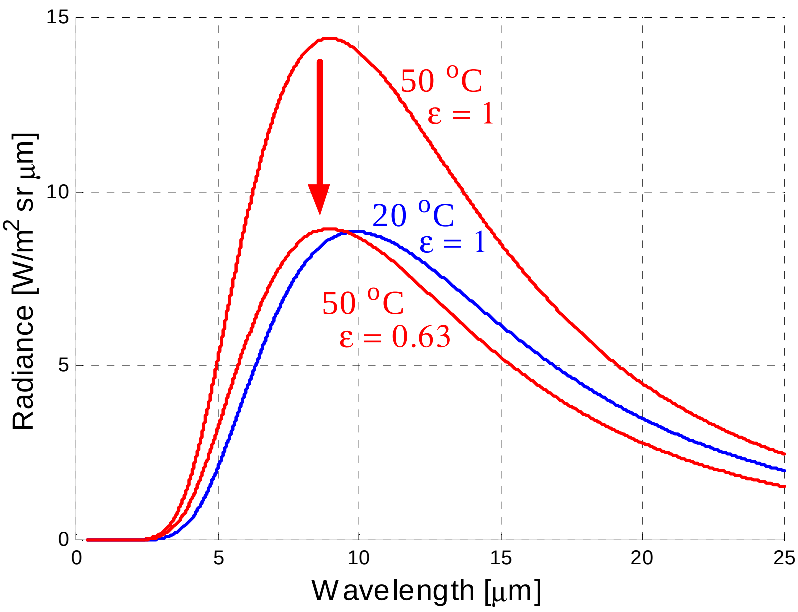

Figure 1. Black body radiation curves for 50ºC and 20ºC (ε=1) and the effect of decreasing the emissivity, resulting in a lower apparent temperature.

Signature suppression of heated surfaces can be achieved by increasing the reflectivity of the surface, since such a surface will have a low emissivity according to Eq. (2). This will decrease the heat radiation from, e.g. the body of a vehicle heated due to internal or external heat sources.

The effect of decreasing the emissivity is illustrated in Figure 1. The radiance vs. wavelength of surfaces at T=50ºC and at T=20ºC, both with ε = 1 (i.e. blackbody radiators), is plotted in Figure 1. In the same plot is also shown the effect of decreasing the emissivity of the high temperature surface, in such a way that its apparent temperature will equal that of the low temperature surface, e.g. the temperature of a background. For camouflage in the visual region it is easy to understand that the object to be camouflaged should have a similar colour and texture as the background, in order to become "invisible". For the IR region the colour in the visual region is replaced by thermal radiation.

The drawback of using highly reflecting surfaces for thermal signature suppression is that external radiation sources like the sun (below 4 µm) and cold radiation from the clear sky (8-12 µm range) may be reflected into such surfaces, as seen by a sensor. Laser-based range finders and radars will also be favoured by low-emissive surfaces. This could be solved by using very diffuse surfaces or by orienting surface segments or pigment flakes at certain favourable angles, as seen from a typical threat direction, in a similar way as in radar stealth design.

In order to obtain a low emissivity in the IR, particles or flakes of a high reflectance in the IR should be used. This is normally achieved using different metals. Since the reflectance properties also are dependent on the particle size distribution, due to wavelength dependent scattering mechanisms, this will also have to be considered. Also, the shape of the pigment particles and their surface structure will affect the reflectance. The problem with metals is that they have a high reflectance in the visual range, which will decrease the visual camouflage effectiveness. However, the application of oxide coating on the pigment could absorb visual light while maintaining a high IR reflectance. This is also achieved by using silicon pigments, since light of energies above the silicon bandgap is effectively absorbed by the material. Pigmentation flakes of multiple-layered structures could also be used to decrease the visual reflectance, for which the reflection properties can be designed using commercial software tools and fabricated by various thin film deposition techniques. Such structures could also be designed in order to avoid solar reflections in the IR. Another group of material structures, which will allow design of the reflectance properties in different wavelength bands, are the so-called photonic crystals. However, such have not been used as a pigment in this investigation.

One important question is what the IR emissivity value of camouflage paint should be in order to blend in with a typical background. An optimal value could be obtained from modelling and measurements. However, in this work we aim to reach as low emissivities as possible since this value can easily be increased as needed. In this work an emissivity of about 0.4-0.6 is considered to be acceptable.

Measurements and samples

The spectroscopic measurement results presented in this work were obtained using a few different spectrometers. For the visual-near IR range a Cary 5G and a Perkin Elmer Lambda 900 spectrophotometer were used, and for the IR range a Bruker IFS 55 FTIR spectrometer. All were equipped with integrating spheres and standard reference samples for calculating the diffuse reflectance. We also used spectroradiometers SR 5000 and SPR314 for determining the emissivity of our samples as a function of wavelength, with the samples mounted on a heated water bath and using a black body radiator as a reference, integrated in the water container. The emissivity was also measured using the FTIR spectrometer by calculating ε from ρ according to the expression in Eq. (2). Similar emissivity values were obtained from the spectrometer and spectroradiometers when measuring the same sample.

A LEO 1550 FEG Scanning Electron Microscope (SEM) was used to study size, shape and structure of pigment particles and cross sections of paint layers. Multiple-layered structures were fabricated by DC magnetron sputtering (Nordiko model 2000) in a vacuum chamber. Paint was produced using a Dispermat SL 503 continuous operation laboratory bead mill. The paint was applied to metal substrates using paint applicators.

Results and discussions

Binders

One of the most critical steps when developing a low-emissive paint for the IR region is the absorption property of the binder material. The absorption of the binder has to be as low as possible, otherwise the radiation that enters the paint layer will be absorbed in the binder, rather than reflected by the IR pigment and transmitted back out through the paint surface. Here we make the distinction between IR pigment, which reflects IR radiation, and pigment that gives the visual colour of the paint. Most regular paints, available commercially, are not optimised for the IR properties that we are interested in here, not even most camouflage paints. One exception is the near IR (NIR) properties, which in some cases will show an increased reflectance in the 0.7-3 µm range, sometimes in order to match the reflection properties of chlorophyll. Examples of reflectance values for a few different camouflage paints and of a birch leaf are shown in Figure 2.

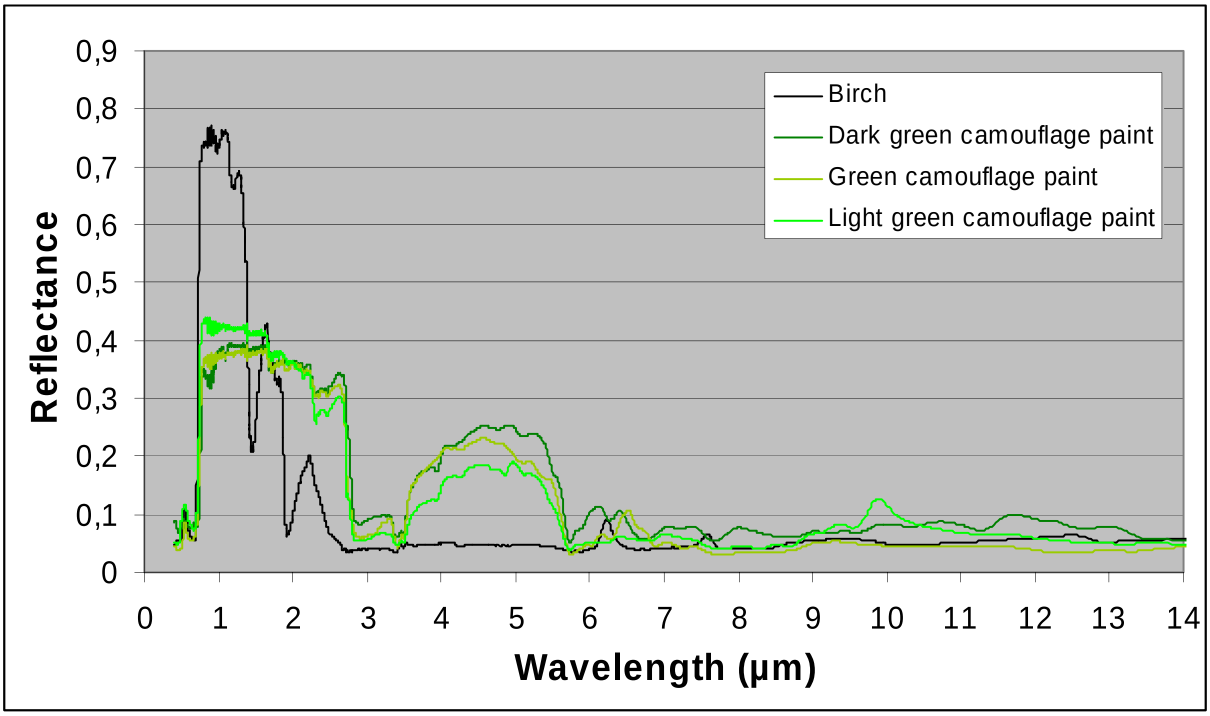

Figure 2. Reflectance vs. wavelength for different camouflage paints.

Most importantly the binder absorption has to be low in the two atmospheric transmission windows at 3-5 and 8-12 µm, where military and other surveillance IR sensors systems operate. Thus, outside of these windows the emissivity of the paint does not have to be low. In fact, by having a high emissivity (i.e. low reflectance) outside the transmission windows, one will allow cooling of a surface by radiation without the risk of being detected, at least not at a longer range.

Various types of polymer-based binders (such as polyurethanes, vinyl polymers, silicone polymers, epoxy resins, polyethylene, chlorinated polyolefine) were characterized in order to find one with good transmission properties. Some of these results were presented in [7]. Typically, in the case of polymers, the absorption in the 3-5 µm region is low as compared to the 8-12 µm region. In 3-5 µm there will in most cases be absorption bands due to C-H vibrations, but sometimes also due to O-H. In 8-12 µm there is typically more and stronger bands present, due to vibrations from C-H, C-N, C-O, Cl-C, C-C and Si-O (for silicone polymers).

A few different water solvable crosslinking polymer dispersions were obtained from BASF, assigned as butyl acrylate or methyl acrylate copolymers. The film formed is colourless, visually transparent and tack-free at room temperature. The absorption spectrum of one of these, in the form of a polymer film, is shown in Figure 3. The absorption bands were identified as due to bend and stretch modes caused by C-H, C-O and C-O-C bonds. The spectrum in Figure 3 most closely resembles that of a polymethyle acrylate, such as poly(methyleacrylate-alt-ethylene) or poly(methyleacrylate-alt-propylene) [8]. This polymer binder was selected and used in order to make different samples of paint using a variety of IR pigments.

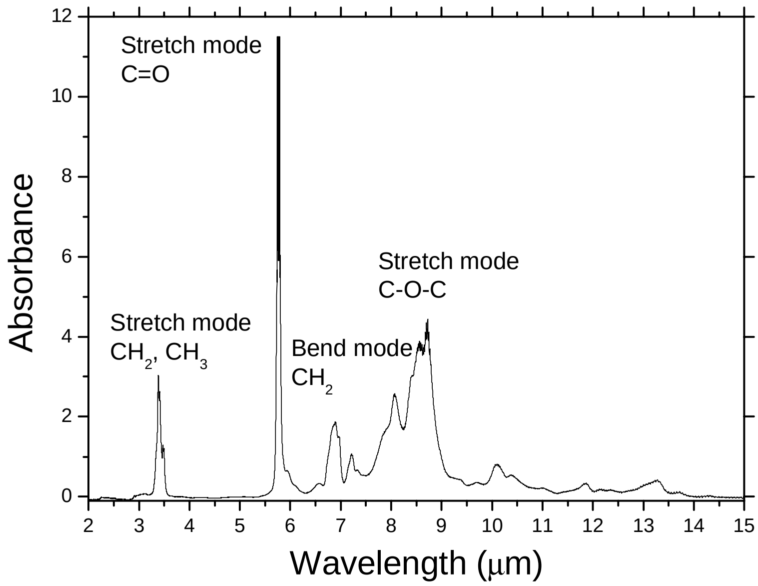

Figure 3. Spectrum of a binder (as a polymer film) obtained from BASF. The absorption bands were identified as different stretch and bend modes according to the figure and from these absorption features assigned as a polymethyle acrylate.

Except for the IR reflective pigment and the binder, the paint should include many other ingredients or additives which will improve various properties of the paint, such as: solvent (water), thickener, coalescent, dispersing agent, antifoaming agent, extender, anticorrosion agent, and different kinds of colour pigments for the visual camouflage. In our experience, these additives will slightly increase the emissivity of the paint by about 10 %. Thus, it is important not to use more additives than necessary.

Pigments

Different IR pigments were spectroscopically characterized, both as a powder and as mixed in a paint. These were pure metals of Al, Ag and Cu, metals with surface coatings (AlO(OH) on Al and AgS on Ag), multiple-layered structures of TiO_2/Au/TiO_2, silicon powder and metal coated cenosphere particles. Figure 4 shows SEM pictures of Al flakes and cenosphere particles (uncoated). Coated metals have been used in order to decrease the reflectance of visual light. In this case, e.g. a metal oxide will absorb visual light, while IR light of a longer wavelength will pass through the coating and be reflected by the underlying metal, as illustrated in Figure 5. The AgS coating was produced in a solution of Na_2S and the AlO(OH) in a solution of NaOH.

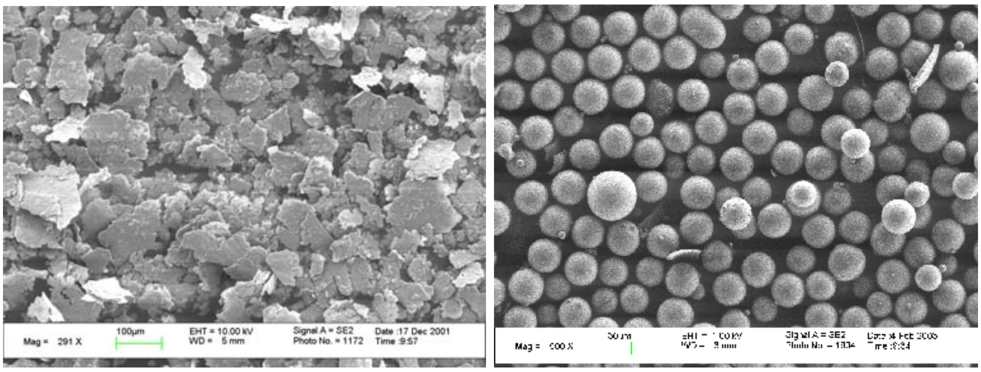

Figure 4. SEM picture of Al flakes (left) and uncoated cenosphere particles (right).

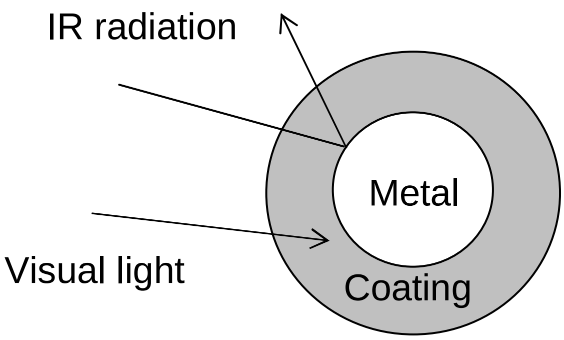

Figure 5. The coating (e.g. oxide) absorbs visual light while transmitting IR light which is reflected by the metal.

The multiple-layered structures were designed to minimise the reflection of visual light while giving a high reflection of IR light. The structure was optimised using a commercial optical coating design software (Film 2000). The physical principle behind this is destructive and constructive interference of light, due to the difference in refractive index between combinations of quarter wavelength thin (optical thickness) layers of metals or dielectrics. In this case we used films of TiO_2 and Au with thicknesses of about 30 and 20 nm, respectively, of three layers (TiO_2/Au/TiO_2), as illustrated in Figure 6. These were produced by sputtering, where the multiple-layers were sputtered on PMMA substrates and divided into flakes when removed from the substrates after being sputtered [6].

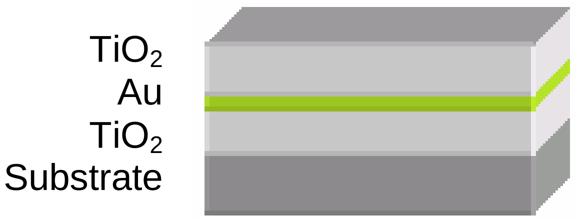

Figure 6. The multiple-layered structure consists of nm-thin layers of TiO_2 and Au, sputtered on a substrate.

Another method to reduce the reflectance in the visual is by using silicon powder. Si transmits light rather well in the IR, except for around 10 µm where Si-O absorbs most of the radiation. As IR radiation falls on Si powder, light which transmits through the Si grains will be reflected at each Si-air boundary (or Si-binder boundary in a paint). This will cause a rather strong backscattering effect, resulting in high reflectance. The higher the difference in refractive index between particle and surrounding medium, the stronger the backscattering power will become. This principle is illustrated in Figure 7. The same effect occurs with grains of sugar and salt in visual light, making the grains look white though individual grains are colourless, i.e. transparent. However, due to the so-called bandgap of silicon, light with wavelengths shorter than about 1.1 µm will be absorbed by the Si powder, making it look dark in visual light.

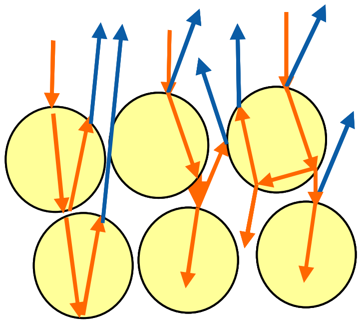

Figure 7. Principle for backscattered reflectance for transmitting particles.

Cenosphere particles have been coated with different metals. A cenosphere is a lightweight, inert and hollow sphere comprised largely of silicon dioxide and aluminium oxide. It is filled with various kinds of gases, such as CO_2 and N_2. These particles are used mainly for the purpose of producing a lightweight pigment. We have coated the cenospheres using different deposition techniques, such as chemical deposition, thermal evaporation and sputtering. Here we present results of cenospheres coated by silver, as obtained in a chemical solution of $AgNO_3$ and NaOH.

Measurement results

Results from measurements of different IR pigments and of these as mixed in paint are summarised in Table I. Note that the results are presented as reflectance for the pigments and as emissivity (1-ρ) for the paint samples.

Table I. Measured reflectance values of IR pigments and emissivities of paint. The values were obtained by taking the average within each wavelength region and among several samples. The paint contained about 20 % pigment (by weight). The asterisk indicates paint including green pigment. The pigment of the 18 µm Al flakes were in the form of a paste.

Pigment	Particle type and size	Refl. of pigment (%)		Emissivity of paint	
		3-5 µm	8-12 µm	3-5 µm	8-12 µm
Al	Flakes, 12-37 µm	-	-	0.34	0.45
Al*	Flakes, ~18 µm	75	70	0.45	0.53
Ag	Powder, >20 µm	75	75	0.8	0.97
AgS	Powder, >20 µm	75	75	0.8	0.93
Cu	Powder, 20-50 µm	-	-	0.7	0.85
Multiple-layer	Flakes	60	60	0.65	0.75
AlO(OH)	Flakes, 18 µm	55	45	0.48	0.62
Si/Al	Powder/flakes	-	-	0.5	0.6
Si	Powder, <20µm	75	50	0.7	0.85
Ag/cenosphere	Powder, 36-45 µm	65	62	0.8	0.9

Pure metal pigment samples

Some different metal pigments were initially used to produce paint without any special additives. These included non-leafing particles or flakes of aluminium, copper and silver. The results are presented in Figure 8. These results, as well as later experiences on different IR reflecting pigments, show that only aluminium pigments, in combination with polymer based binders, give rise to an acceptably low emissivity. There may be several reasons for this. One basic property, which controls the reflectance or the emissivity of the paint, is the refractive index difference between the pigment and the binder. The refractive index of the BASF binder polymer was determined by using IR ellipsometry to a value of about 1.45-1.50. However, when calculating ρ from the refractive index of the binder material and the different pigments, it can not explain the high emissivity over such a broad spectral range. Another explanation could be that some chemical reaction occurs between the binder and the IR pigment. It is well known that aluminium has a very stable natural oxide layer on top of the metal, which could explain why paint with Al pigment is not affected. The differing results among the Al pigments should mainly be explained by two different reasons; particle size dependent scattering and surface structure/shape dependent scattering. If the surface area is increased due to an irregular surface structure, the emissivity will increase.

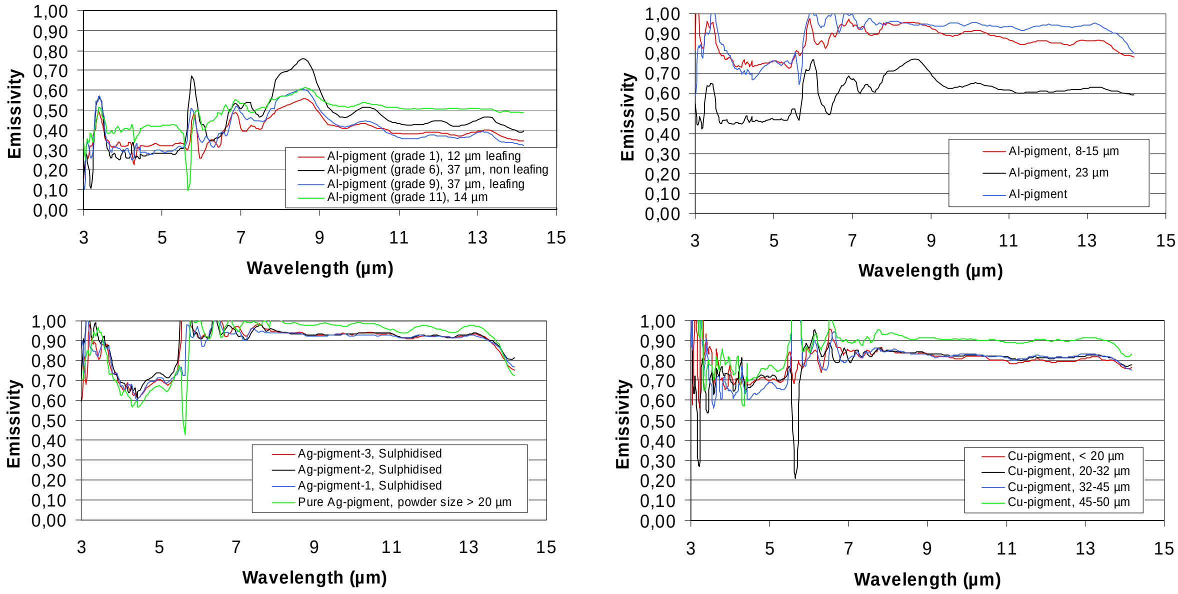

Figure 8. Emissivity measurement results of paint samples composed of different metal pigments. No additives were included in the paint except for the binder and solvent (water).

The plot to the left in Figure 9 shows results from reflectance measurements on Al flakes, originally as a paste of waterborne pigment. The average flake size was 18 μm. Prior to measurements the paste was either dried on a substrate or dried in a furnace at 450 ºC in a flow of O_2 gas and then measured as a powder. The lower reflectance of the paste dried in a furnace is probably caused by the agglomeration of flakes. The plot to the right in Figure 9 shows measurement results of green paint samples, including Al flakes with concentrations of 7.5, 10, 15 and 20 % (by weight). These results are quite satisfactory since they show that it is possible to obtain a rather low emissivity. Also, it shows that the density of the IR pigment can easily adjust the emissivity of the paint. Paint with Al flakes, with an average size of 10 μm was also made, showing a higher emissivity by about 0.15-0.25 as compared to the 18 μm flakes. These two different kinds of flakes were only different in respect to size.

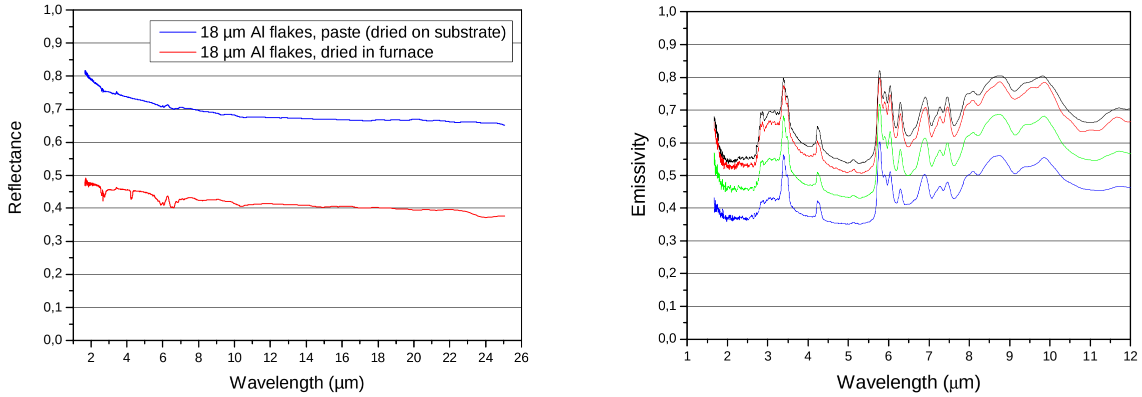

Figure 9. Reflectance of 18 µm Al flakes (left plot) and emissivity for a green paint (right plot) with different concentrations of Al flakes (7.5, 10, 15 and 20 %, in that order producing high to low emissivity).

Other results of green low-emissive paint samples are shown in Figure 10. Both samples contained 20 % Al pigment (18 µm flakes), while one (KOE 153) contained three different additives in order to improve the film formation properties, which were not included in the other sample (KOE 180). Pictures of these samples are presented in Figure 11, showing that the sample with the three extra additives (left picture) is slightly lighter in colour as compared to the other.

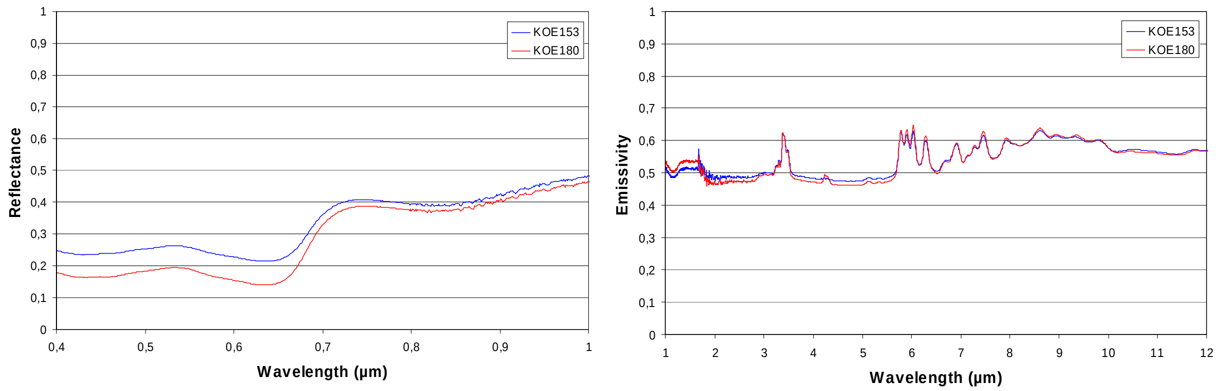

Figure 10. Reflectance in the Vis-NIR (left) and emissivity in the IR (right) of green camouflage paint samples KOE 153 and KOE 180. The samples contained 20 % Al pigment. KOE 153 contained 3 extra additives in order to improve the film formation properties.

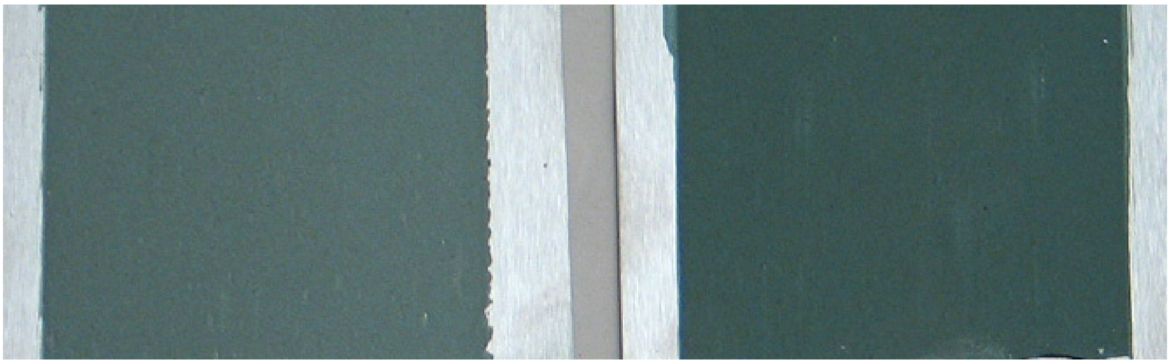

Figure 11. Pictures of low-emissive green paint samples including Al flakes (KOE 153 left sample, KOE 180 right sample).

Cenosphere particles were coated with silver from a chemical solution of $AgNO_3$ and NaOH. The metal layer on the cenosphere was thick enough in order to get an optimal reflection without any losses due to transmission through the metal. Other deposition techniques and metals have also been tested [4]. Reflectance measurements of Ag coated and non coated cenosphere powder are presented to the left in Figure 12, showing that the coated cenospheres have the potential of giving rise low emissivity of paint. However, to the right in Figure 12 it is shown that such paint has a rather high emissivity, similar to the results of regular Ag powder in Figure 8.

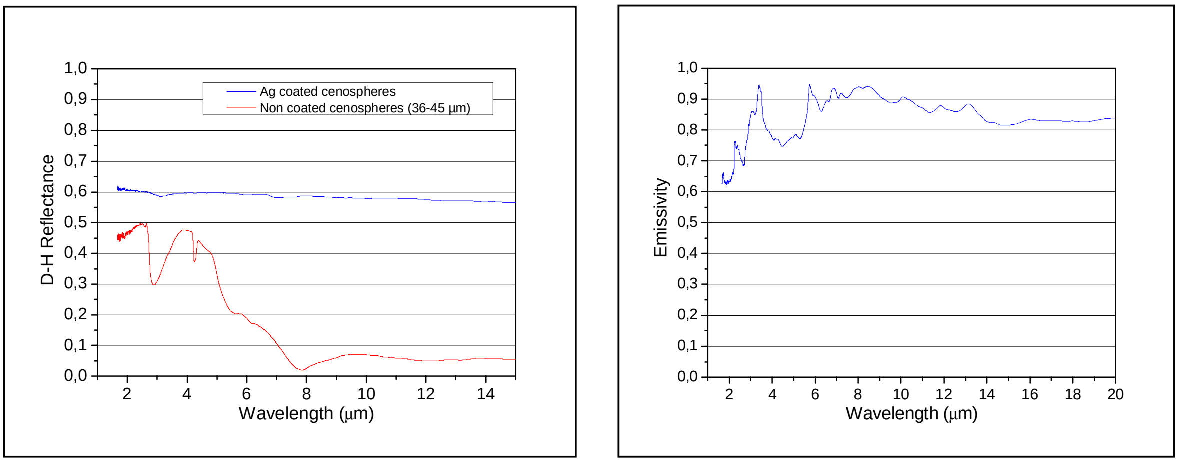

Figure 12. The left plot shows the reflectance properties of coated and non-coated cenosphere powder and the right plot the emissivity of paint with Ag coated cenospheres.

Pigments with surface coatings

As mentioned earlier, the drawback of pure metal pigments such as Al, is their rather high reflectance in the visual region. In order to avoid, e.g. unwanted reflections from the sun, the IR pigments should have a minimal reflectance in the visual range. To obtain this, different techniques may be used, such as various surface coatings (e.g. oxides) on metals, powder of IR transmitting semiconductors, such as Si or Ge, and special design of multi-layered structures.

The picture in Figure 13 shows samples with different visual reflectance achieved by using a AlO(OH) layer on Al flakes, by mixing Si powder with Al flakes and by using Si powder. A sample with pure Al flakes is shown as a reference. The spectroscopic measurement results of these samples are given in Figure 14. The left plot shows how the visual and NIR reflectance is affected by the different pigments, where the pure Si powder reduces the reflectance rather dramatically due to the Si bandgap. The plot to the right in Figure 14 shows that all but the Si paint sample have acceptably low emissivity values.

Results from some other pigments listed in Table I which reduce the visual reflectance, i.e. the AgS coated silver powder and multiple-layered flakes, did not give acceptably low emissivity values when mixed in the binder. The paint of the AgS coated silver powder showed a very high emissivity, according to Figure 8. However, the results in Figure 15 (right plot) of paint including multiple-layered flakes was slightly better. The left plot in Figure 15 shows that the design of these flakes was successful, in such that the visual reflectance is low, except for a slight increase in the blue-green region, while the reflectance increases in the NIR region and remains high throughout the IR.

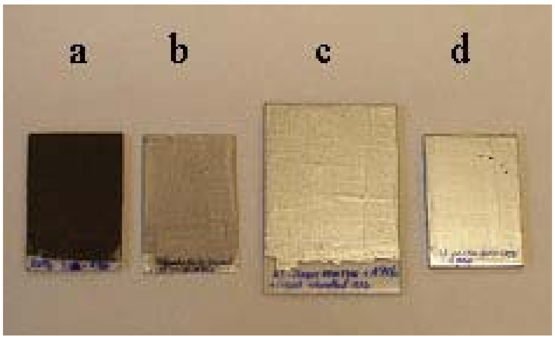

Figure 13. Picture of paint samples with different visual reflectance values, caused by the difference in IR pigments. (a) Si pigment, (b) Si and Al pigments mixed 50/50, (c) Al pigment with AlO(OH) coating and (d) pure Al pigment.

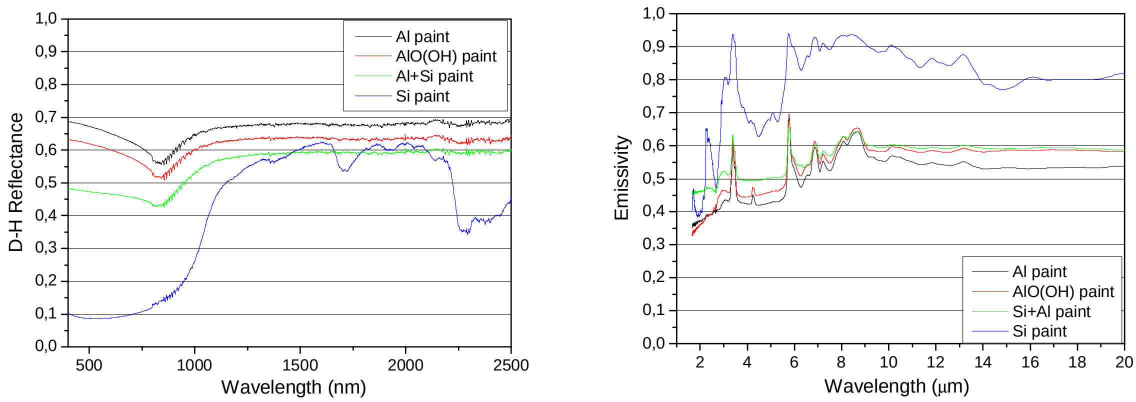

Figure 14. Reflectance (left plot) and emissivity (right plot) for paint samples containing different IR pigments in order to reduce the visual reflectance.

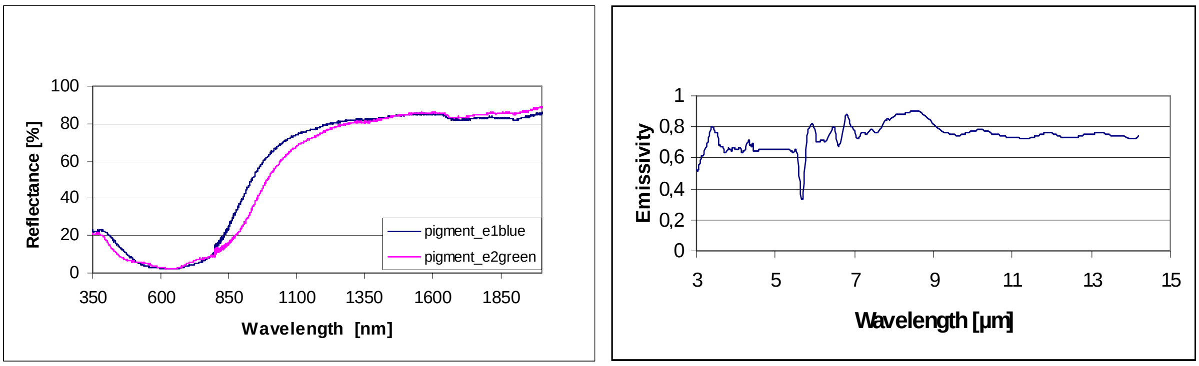

Figure 15. Measurement results of the multi-layered pigment. The left plot shows the reflectance of the pigment flakes in the Vis-NIR region, and the right plot shows the emissivity of the paint in the IR region.

Radar transmission measurements

An analogue network analyser (Wiltron 37269B) was used for measuring radar transmission through paint samples in the 8-12 GHz range (X band). In this case paint was applied on plastic substrates (PMMA), instead of metallic substrates, in order to be able to carry out transmission measurements. The average transmission of the PMMA substrates in the X band was about 70

%. For a layer of paint, similar to that presented in Figure 9 and Figure 10, including 20 % Al flakes and green pigments, the average transmission was found to be 73 %. For paint without additives containing 15 % of IR pigment (Al flakes, metal coated cenospheres or Si powder) a transmission of 95-96 % was obtained.

Conclusions and summary

Different kinds of IR pigments, i.e. pigments having a high reflectance in the IR, have been characterized and used in order to develop low-emissive camouflage paint. Some of these IR pigments were developed in order to obtain special characteristics, such as low reflectance in the visual wavelength range (in order to decrease sunlight reflections) and lightweight pigments. The binder material used was obtained from BASF and was an aqueous polymer dispersion that crosslinks during film formation. To solve the main problem when developing a low-emissive paint, it is necessary to find a binder that is transparent enough in the IR. The binder used here was found to have a rather high transmission in the IR, with the main absorption in the 8-9 µm range. Various additives were also included in the paint to improve its properties. Colour pigments were added to obtain a green colour.

Only paint consisting of Al pigments showed a sufficiently low emissivity, although the reflectance from all of the pigments themselves was found to be high. The reason for this is not known. Other binder materials could perhaps be more suitable for these other IR pigments. An emissivity of about 0.4 in the 3-5 µm range and about 0.5 in the 8-12 µm range was obtained for green paint with 20 % (by weight) Al pigment. The higher emissivity in the 8-12 µm range is due to absorption of the binder and derives also from some of the additives.

It is important to maximise the radar transmission through camouflage paint in case it is to be applied on RAM surfaces. The transmission in the X band was found to be above 70 % for all paint samples measured.

As mentioned previously, the paint should also undergo different trials in order to determine the effects of weather, how cleaning will affect the IR and visual reflectance properties, and mechanical and physical properties of coatings. However, these trials have not yet been performed.

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