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Report title

Multilayer structures for low emissive paint

Abstract (not more than 200 words)

This report describes the preparation of pigment for low emissive paint. In order to determine the optical properties of the pigment calculations are done with the commercial software, FILM 2000, from Kidger Optics in England. Suitable materials were decided and a 3-layer structure was accomplished by sputtering. Thereafter the coating was removed from the substrate. Reflectance measurements were made on the substrate coated with a 3-layer structure and on the flakes removed, both in the visual and the IR-region. The flakes were sent to collaborators at DFRIT in Finland where the paint was fabricated and evaluated.

Keywords

Thermal infrared, pigment, camouflage paint, low emissive

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Rapportens titel (i översättning)
Multilagerstrukturer för lågemissiv färg

Sammanfattning (högst 200 ord)
I denna rapport beskrivs tillverkningen av pigment för lågemissiv färg. För bestämning av de optiska egenskaperna hos pigmentet har beräkningar gjorts med ett kommersiellt dataprogram, FILM 2000, från Kidger Optics i England. Lämpliga material bestämdes och 3-lager-strukturer tillverkades genom sputtring. Därefter avlägsnades ytskiktet I form av flingor från substratet. Reflektansmätningar gjordes på substrat med 3-lagerskikt och på flingorna sedan skiktet avlägsnats, i både visuella och IR-området. Flagorna skickades till samarbetspartners vid DFRIT i Finland där färg framställdes och utvärderades.

Nyckelord
Infraröd, pigment, kamouflagefärg, lågemissiv

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Contents

1. Introduction

Infrared (IR) sensors are now widely used for various military applications such as surveillance, missile seekers and missile warning systems, for detecting heat emission from hot objects ranging from exhaust plume emission to human bodies or well camouflaged objects. They are also useful when darkness or light fog diminishes the possibilities for detection by a normal eye. The region of detection though, is limited to the transmission windows at 3-5 and 8-12µm, elsewhere the atmospheric gases (H_2O, CO_2, etc.) absorb the radiation.

The recent development of infrared sensors has increased the probability of being detected or identified on the battlefield. The spectral range and resolution of the sensors have increased as well as the spatial resolution and temperature sensitivity. This development encourages the need for more advanced low observable camouflage materials for military vehicles, ships, airplanes, textiles etc.

One way to reduce the possibility of being detected, is the use of surface modification. It has been suggested that a surface can be modified with a low emissivity paint, to achieve a low temperature appearance [1, 2]. Paint was proposed rather than other forms of surface modification since paint can quite easily, and at low cost, be applied to surfaces. Today's conventional paints normally have a low reflectance in the IR region, hence some investigation into this field is in place.

Paint consists primarily of pigment and a binder. The pigment may be in the form of powder or flakes of a low emissivity material. By low emissivity we normally mean a surface that radiates considerably less as compared to a blackbody held at the same temperature. Thus, such a surface would reflect the properties of its surroundings.

In this report, the reflectance properties of multilayer structures, in the form of films and flakes, are evaluated. Modeling and calculations were made with the commercial software FILM 2000 on several material combinations. Special attention was given to the combination of the dielectric titanium dioxide (TiO_2) and the metal gold (Au), which gives a large difference in refractive index n. This material combination promised a high reflectance in the IR-range and a low reflectance in the visible wavelength range. This is inline with our demands for a matted surface in the visible range and a low emissivity surface in the IR, which is less likely to emit revealing heat as compared to a background.

A three-layer film structure was constructed by sputtering. The film was divided up into flakes, which were removed from the substrate to make a pigment. The pigment was combined with a binder in order to obtain the final paint. The choice of binder, the production and the measured performance of the paint were done at the Defence Forces Research Institute of Technology (DFRIT) in Finland.

Light falling into a surface can be transmitted (t), reflected (r) or absorbed (a) (see Figure 1). The sum of these three terms is equal to the incident light, see equation (1):

$$1 = r + t + a \qquad (1)$$

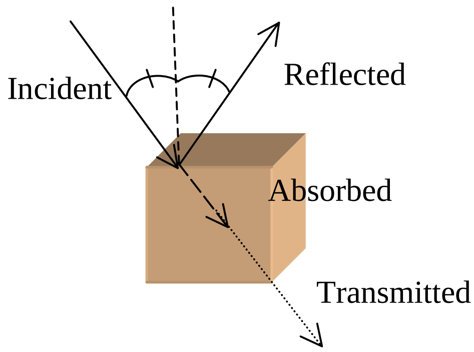

Figure 1.

Light falling into a surface can be transmitted, reflected or absorbed.

The heat radiating from a real surface at a certain temperature and in a particular spectral range is normally smaller than that from a blackbody held at the same temperature. The radiation is given by $E = \varepsilon\, \sigma\, T^4$, where E is the radiation from the surface, ε the emissivity, T the temperature and σ is the Stefan-Bolzmans constant ($\sigma = 5.67 \cdot 10^{-8}$ [W/m^4 K^4]. Emissivity is defined as the ratio of the emission from a sample to that from a blackbody at the same temperature and in the same spectral interval. A blackbody radiator, by definition radiates with an efficiency of 100%. Thus, a blackbody is a perfect thermal emitter.

In the case where light falls onto a material surface that is non-transmitting, the emitted radiation (ε) in the steady state is equal to the part of the radiation that is absorbed, see equation (2):

$$1 = r + \varepsilon \qquad (2)$$

i.e. the emissivity equals $\varepsilon = 1 - r$ (or $r = 1 - \varepsilon$).

2. Calculations

The commercial calculation program Film 2000, described elsewhere [2], was used for determining or optimising the reflection properties of coatings, consisting of multilayer structures of certain thicknesses and material combinations. The refractive index n and extinction coefficient k for the used materials are presented in the table.

(λ_{ref} = 550nm)	n	k
Substrate	1.52	0
TiO_2	2.33	0
Au	0.36	2.69
Air	1	0

Comparison gold and titanium dioxide

A few material combinations were considered. Titanium and gold targets were available and these materials showed promising properties, and were therefore chosen.

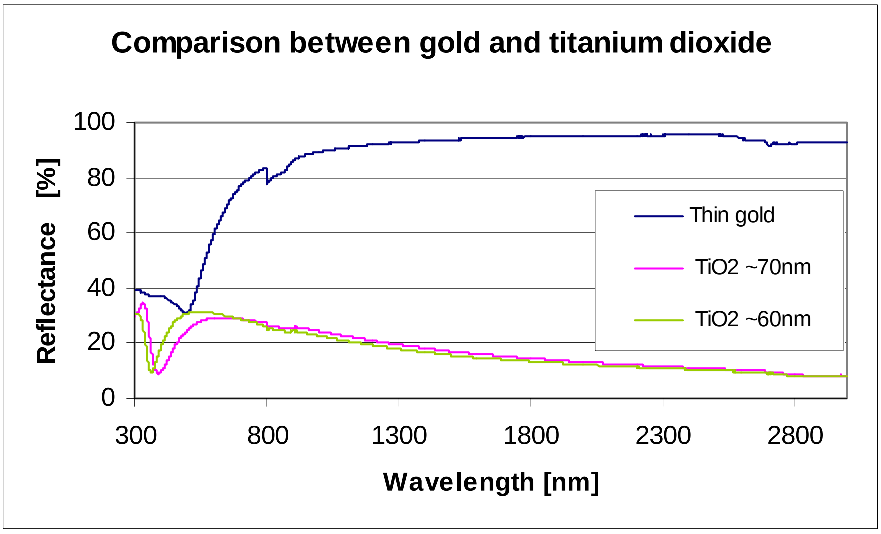

Figure 2
Comparison of reflectance for TiO_2 (two different thicknesses) and gold.

Gold has, as most metals, a high reflectance in the IR-region, and its yellow colour is given rise by a relatively high reflection in the low energy range of the visible spectrum as compared to higher energies. A thin layer of gold will transmit light mainly in the green spectral range, which causes the reflectance dip at 500-600nm in Figure 2. A thin layer of titanium dioxide (TiO_2) on a gold layer will reduce the reflection in the visible region even more, as will be shown later on in this text (see Figures 4-6).

3-layer structures

As a symmetric structure was desired when making the flakes, a titanium dioxide layer was deposited on both sides of the gold layer.

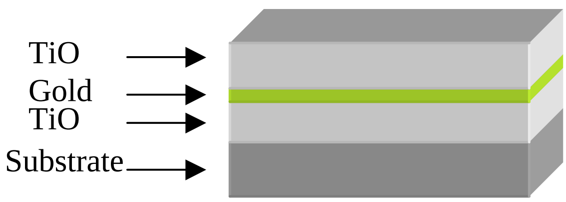

Figure 3 *A 3-layer structure of TiO_2 and Au.*

Calculations and measurements on grown layers were first compared for some different thickness combinations. It was found that the calculations fit quite well with the experimental data, as shown in Figures 4-6.

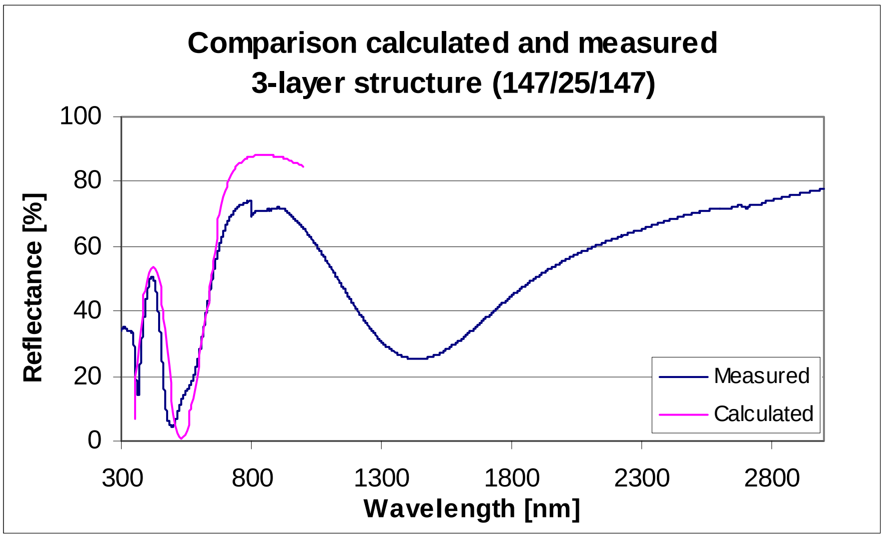

Figure 4
Comparison between calculated and measured 3-layer structure of gold and titanium dioxide (thin gold layer). Thickness given in nm.

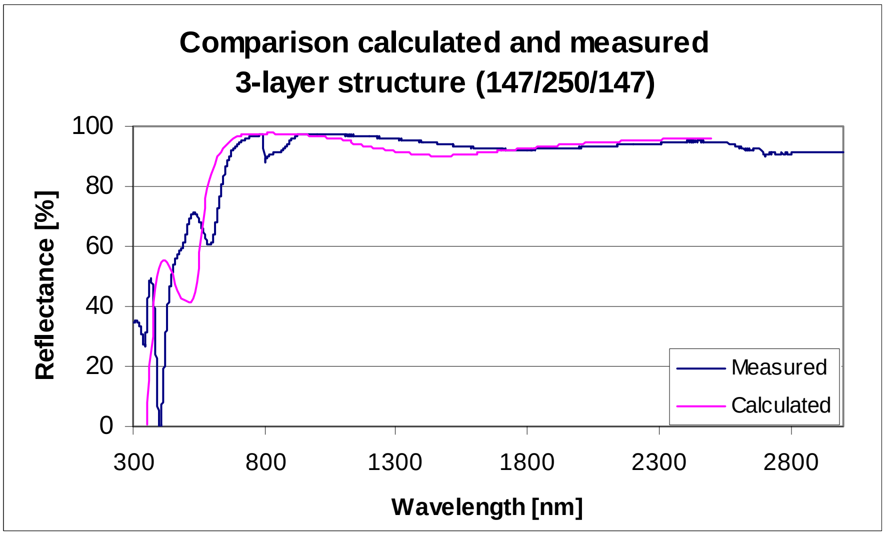

Figure 5
Comparison between calculated and measured 3-layer structure of gold and titanium dioxide (thick gold layer). Thickness given in nm.

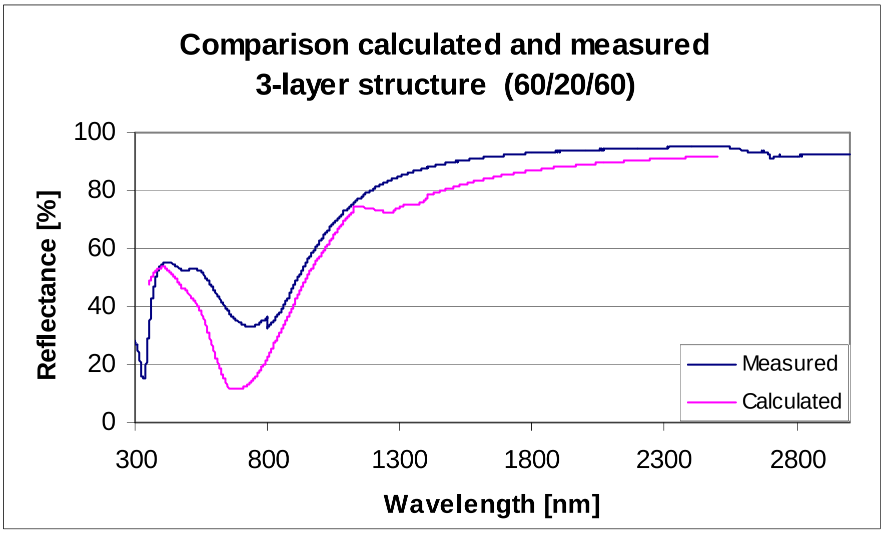

Figure 6
Comparison between calculated and measured 3-layer structure of gold (thin layer) and titanium dioxide (relatively thin layer). Thickness given in nm.

3-layer structures – 30nm titanium dioxide, 20nm gold

The calculations in Figures 7 and 8 show that a multiple layer structure combination of ~30nm TiO_2, ~20nm Au and ~30nm TiO_2 corresponded best to our demands. Calculations were made for a few different angles of incidence form 0° to 60°. In the following of the report only 0° angle of incidence will be used.

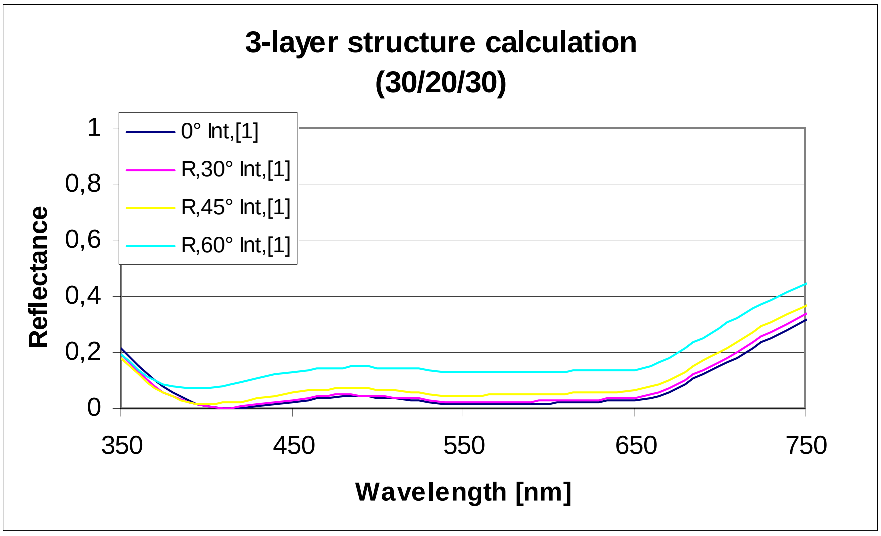

Figure 7
Calculated reflectance in the visible region for a 3-layer structure of TiO_2 / Au / TiO_2. Thickness given in nm.

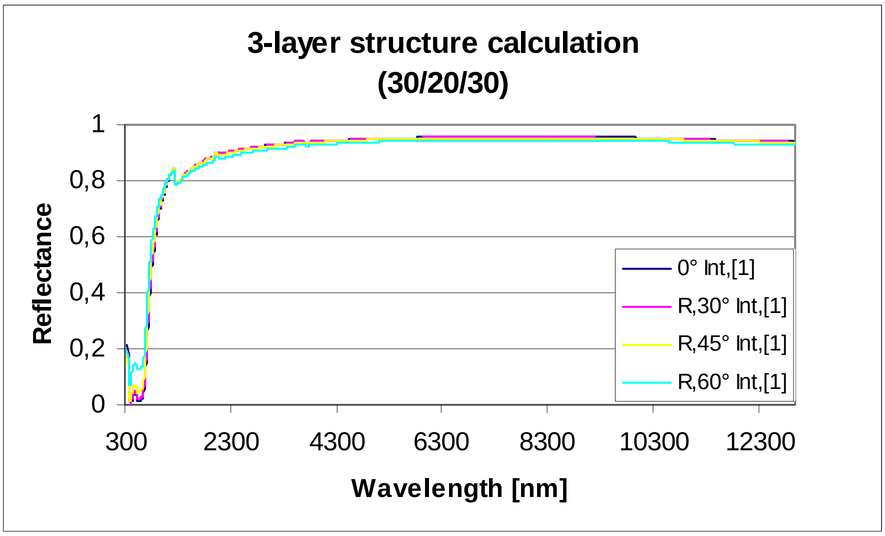

Figure 8
Calculated reflectance in the IR region for a 3-layer structure of TiO_2 / Au / TiO_2. Thickness given in nm.

5-layer structures

There may be several advantages in using more than 3 layers. One is that there will be a sharper change in reflectance between regions of high and low reflectance. Another is that it will be easier to produce flakes from a thick film as compared to a thin, which more easily will break up into a powder. According to Figure 9 the reflectance in the visible region is slightly higher as compared to Figure 7. In Figure 10 the sharper increase in reflectance brings it to a higher level in the near IR region, as compared to Figure 8.

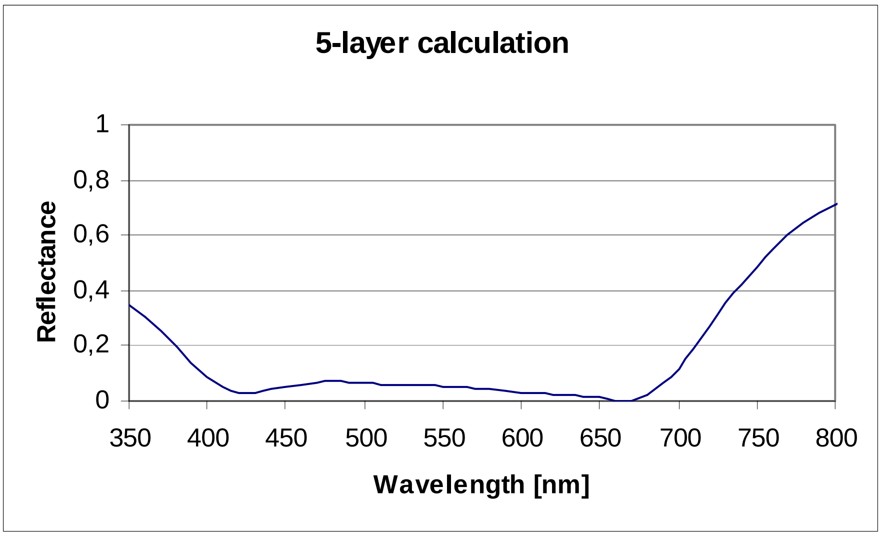

Figure 9
Calculated reflectance in the visible region for a 5-layer structure of TiO_2 / Au / TiO_2 / Au / TiO_2, of thicknesses 30/ 20/ 67/ 20/ 30 nm, respectively.

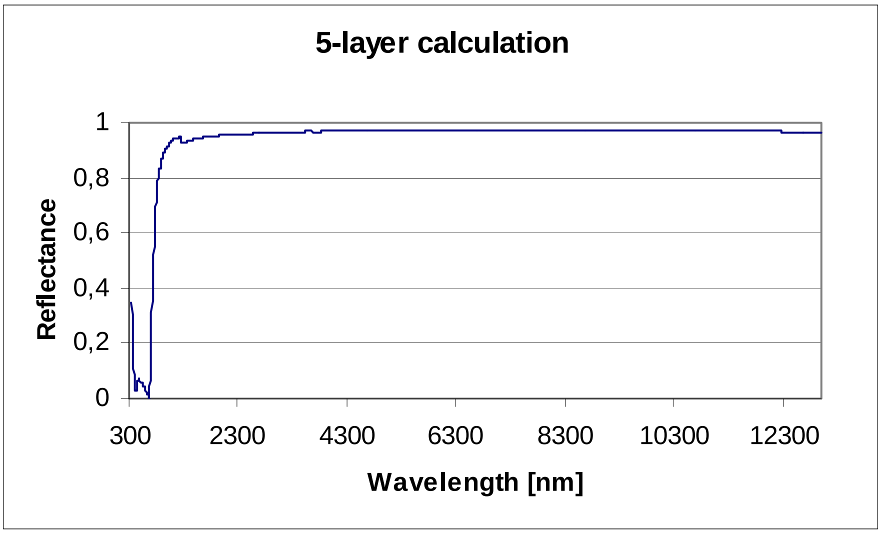

Figure 10
Calculated reflectance in the IR region for a 5-layer structure of TiO_2 / Au / TiO_2 / Au / TiO_2, of thicknesses 30/ 20/ 67/ 20/ 30 nm, respectively.

7-layer structures

Calculations were also made on a 7-layer structure (TiO_2/Au/TiO_2/Au/TiO_2/Au/TiO_2). In the following example the total thickness is about 236nm and the individual layer thicknesses are 24 /20 /60 /20 /60 /20 /32 nm, respectively.

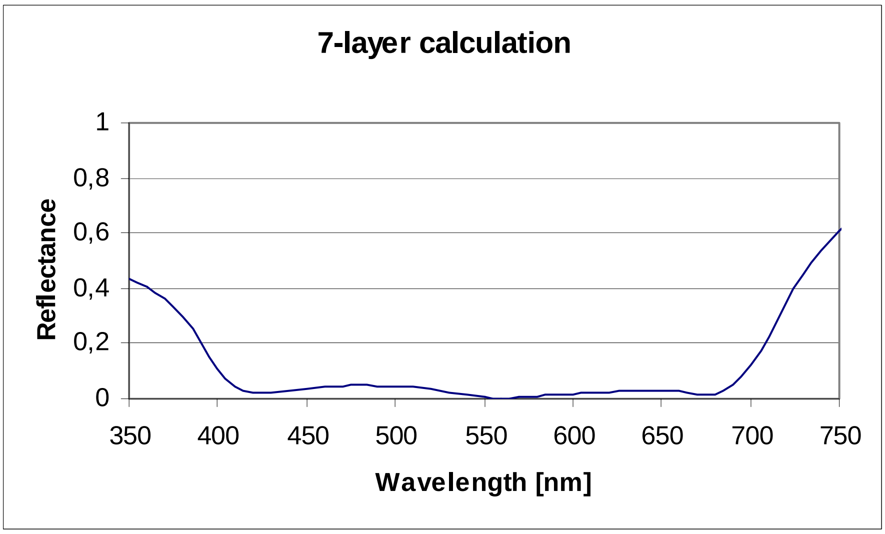

Figure 11
Calculated reflectance in the visible region for a 7-layer, total thickness of about 236nm.

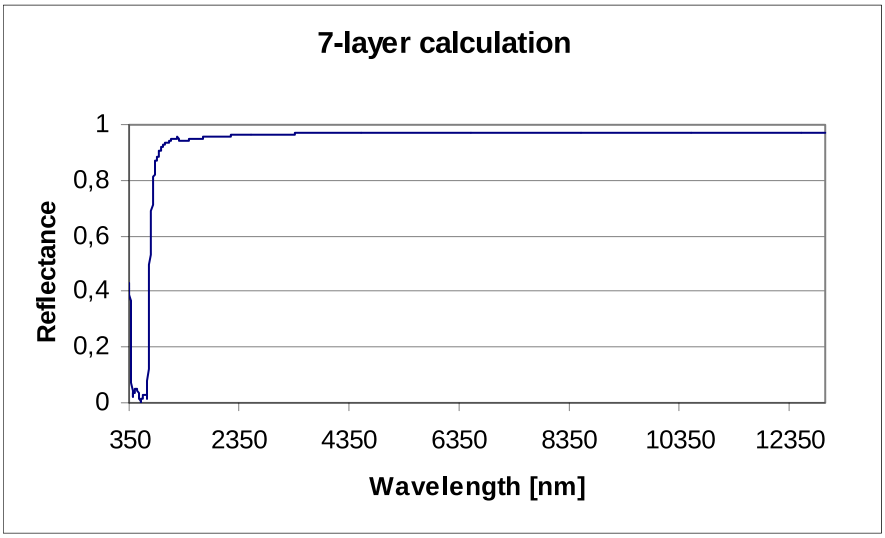

Figure 12
Calculated reflectance in the IR region for a 7-layer, total thickness of about 236nm.

The results shown in Figures 11 and 12 are similar to those of the 5-layer structure, except for some slight differences in the visible region.

3. Production process

Cleaning process

Substrates of Poly(methylmethacrylate) (PMMA) were washed in an ultrasonic bath, in both distilled water and in ethanol and dried before the coating process.

Sputtering

The multiple-layer structure was achieved by using a sputtering process [3] where the argon atoms are separated into ions by an applied potential difference. Material is removed from the target by the Ar-ion bombardment, and is reorganised onto the substrate. This is further explained and illustrated in Figure 13.

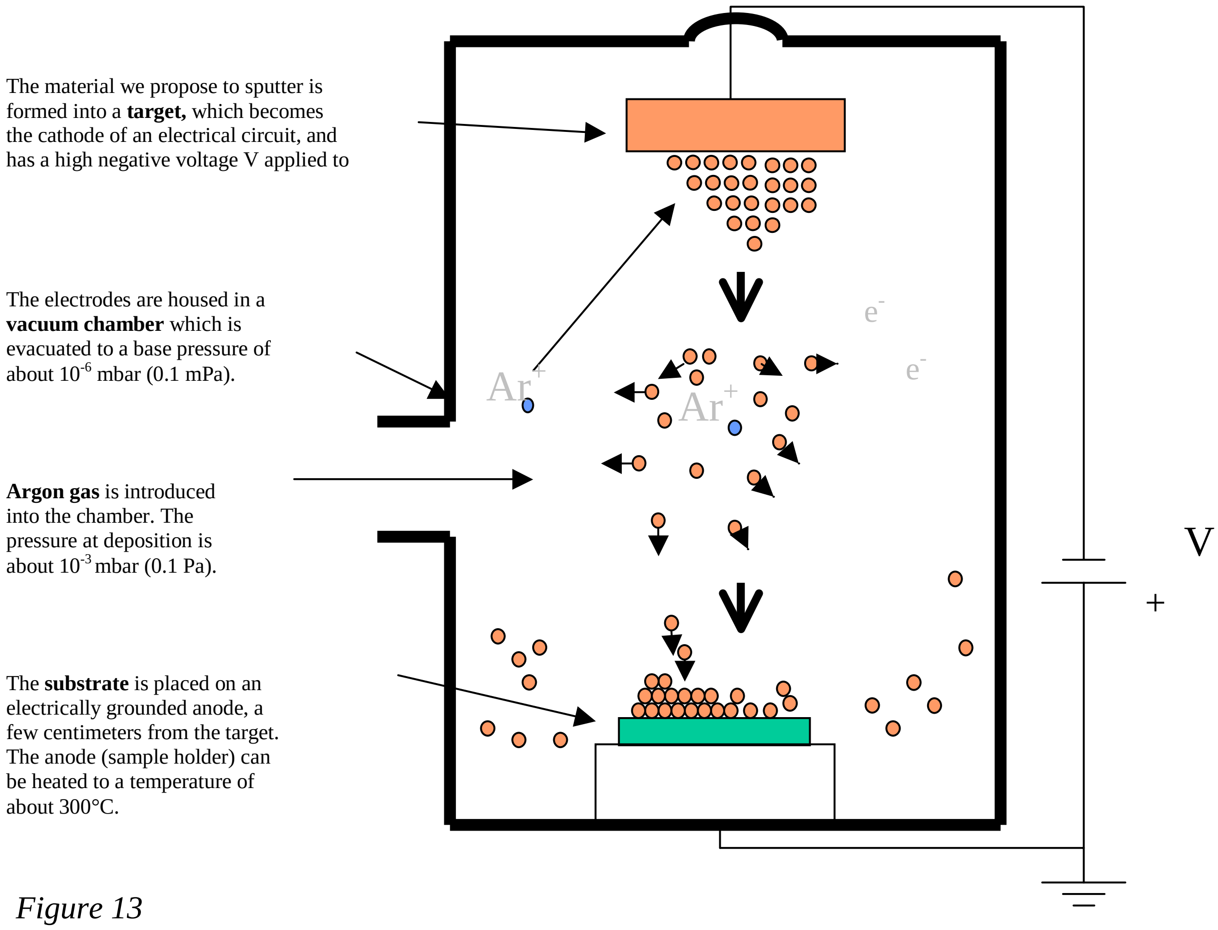

Figure 13
The sputtering process.

The titanium dioxide layer was grown using oxygen as oxidation gas, with 80 units, using a deposition pressure of 10^{-3} mbar. The baking time was 8.5 minutes at 300 W. The gold layer was baked for 8 s, with 15 units of argon, using 150 W, and a deposition pressure of about 7×10^{-3} mbar. The layer thicknesses were measured to be 20nm and 30nm for TiO_2 and gold respectively by using a Dektak^{3}ST surface profileometer from Veeco Instruments Ltd. A special target holder was used so that two substrates could be coated during the same down-pumping session by turning the substrate holder 180°.

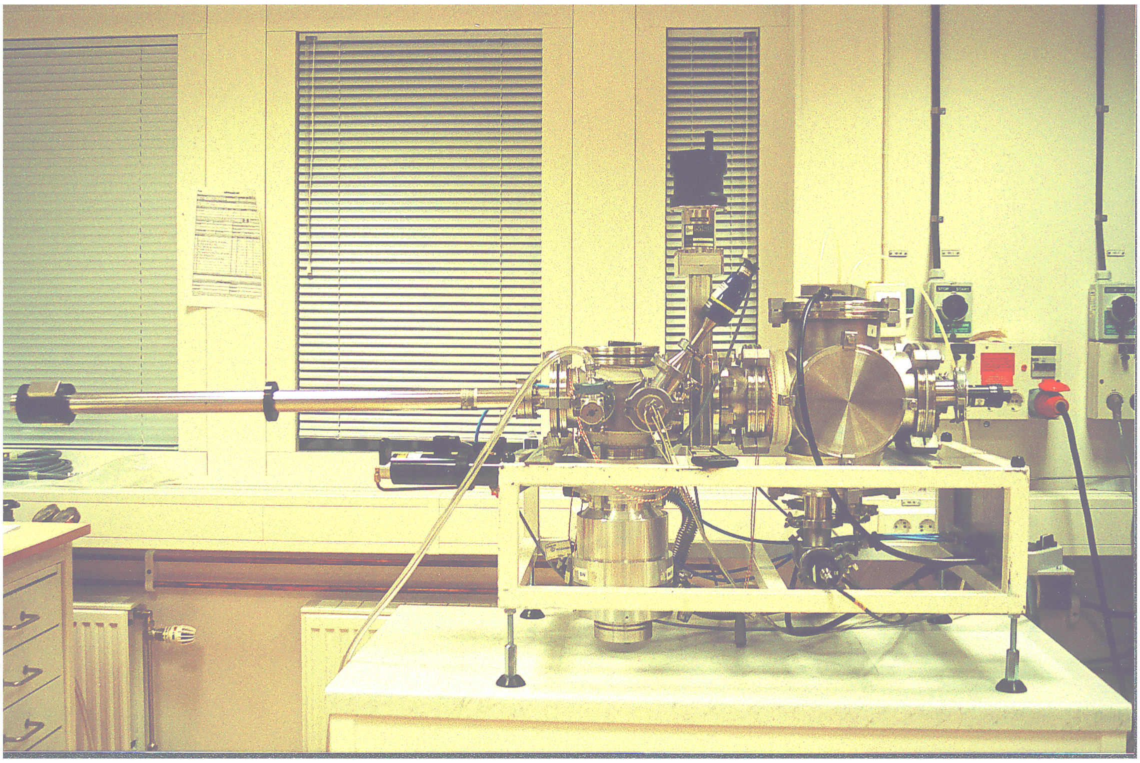

Figure 14
The sputter.

Removal of film from substrate

The coating had to be removed from the substrate in order to get flakes. As ethanol was administered dripwise onto a PMMA-substrate, the multiple layers cracked and could easily be removed mechanically. A test was also carried out on a Polycarbonate (PC) substrate, in which case the film could not be removed, and therefore PMMA was used in all further work. However, in some cases a powder, rather than flakes, was obtained.

4. Measurements

Reflectance measurements were performed using a UV-Vis-NIR Cary 5G spectrometer in the visible region and a Bruker IFS 55 spectrometer in the IR-region. The two graphs in the Figures 15-16 and 19-22 each represents a sputtered substrate, sputtered one after the other under identical conditions with the same settings and adjustments during the same down-pumping session. The measurements in the IR-region were all made using an integrated sphere.

Reflectance for 3-layer films

Reflectance measurements made on the coated substrates showed, for the first sputtered sample (010515-1), good correspondence with the calculated values, see Figures 15 and 16. In the visible region low reflectance levels of about 10-20% were attained, and in the IR-range high reflectance levels of about 70 to 90%. See also Discussion and conclusions. An integrating sphere was used for the measurements in both cases.

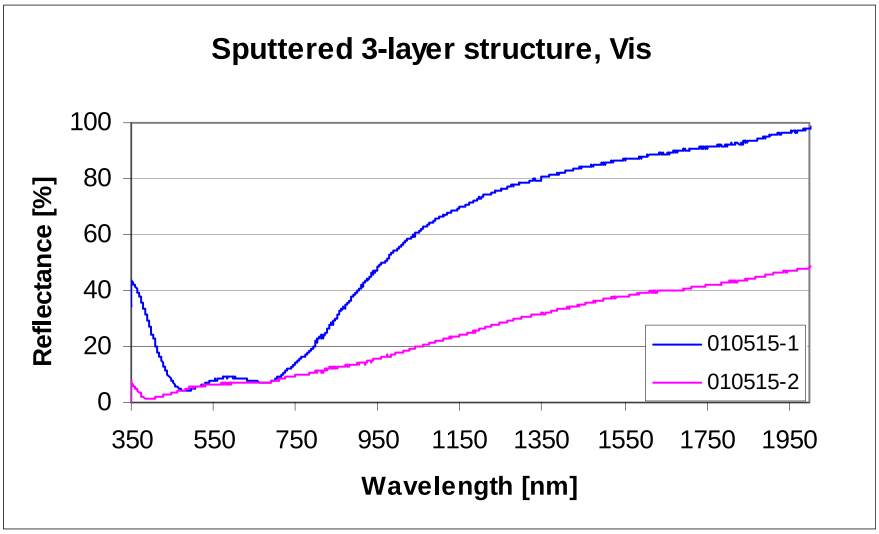

Figure 15
Measurement in the visible and NIR region on a sputtered 3-layer film.

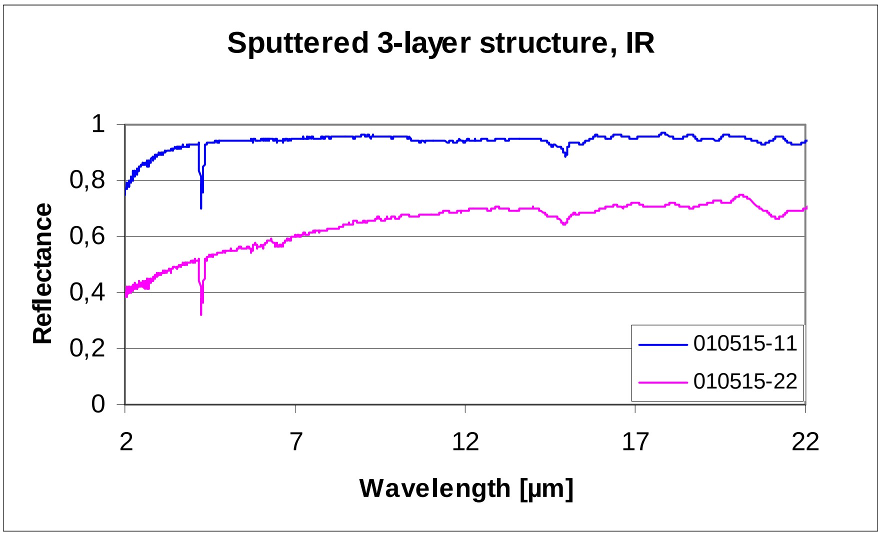

Figure 16
Measurement in the IR-region on a sputtered 3-layer film.

Measurements on pigment made from 3-layer films

Measurements were also made on pigment in the form of flakes or powder. The size of the pigment particles turned out to be difficult to control. By placing the particles in a small cup, the reflectance could be measured in an integrated sphere set-up. The reflectance was found to be quite low, probably due to the small size of the particles and because they were not tightly packed. Neither did it have a smooth surface. Radiation was also possibly absorbed by multiple reflection among the particles/flakes in the surface region. In the visible region reflectance levels of about 10% or less, and in the IR range, levels of about 20-30%, were attained (see Figures 17 and 18, pigment_f).

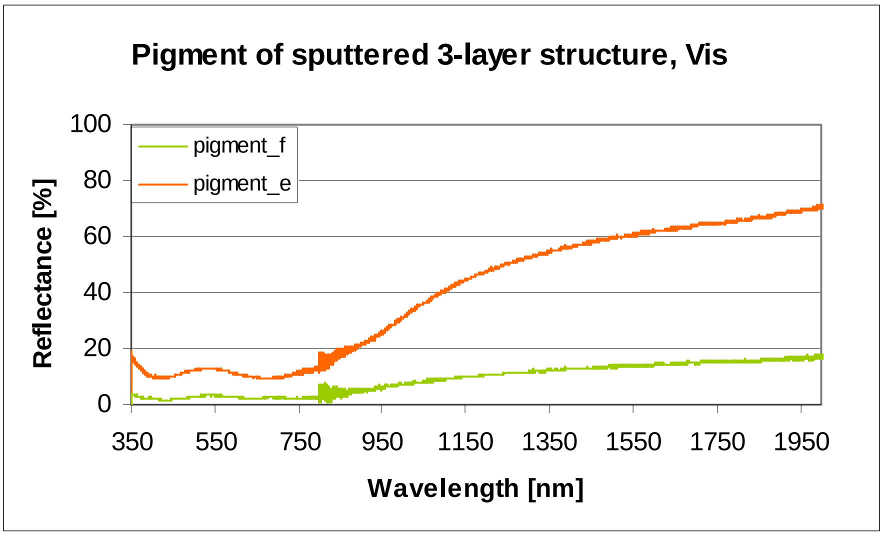

Figure 17
Pigment of 3-layer film, visible range.
pigment_e: the particles are smoothed to a surface by adding a drop of ethanol.
pigment_f: the powder placed in a small cup but not tightly packed.

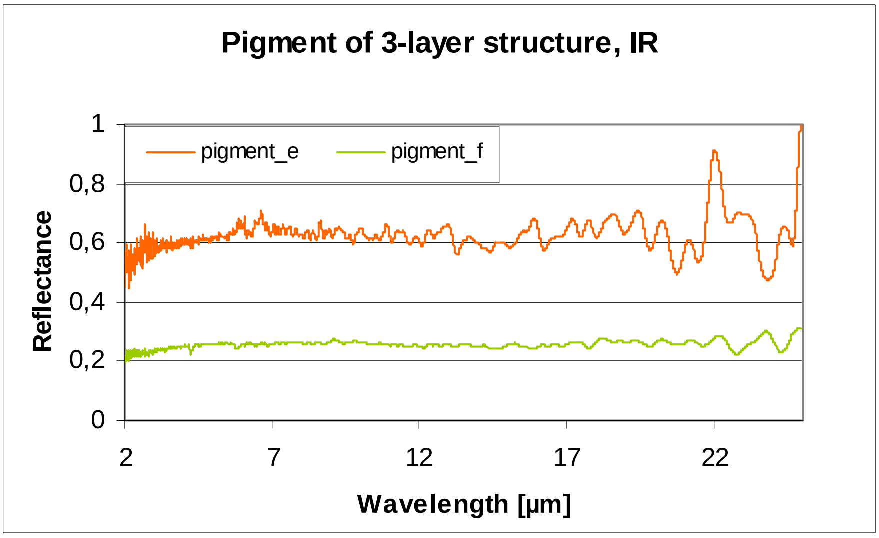

Figure 18
Pigment of 3-layer film, IR range.
pigment_e: the particles are smoothed to a surface by adding a drop of ethanol.
pigment_f: the powder placed in a small cup but not tightly packed.

On the other hand, when spreading the flakes by diffusion on a substrate by adding a drop of alcohol to a pile of pigment, the pigment flakes did not organise themselves in a complete surface coverage of the substrate. However, the surface finish was smoother than without adding the drop of alcohol. In this case the pigment turns green/purple/blue instead of black, and the reflectance properties look more like these of the film (see figure 17 and 18, pigment_e).

Reflectance of 5-layer films

Measurements made on a sputtered 5-layer structure can be seen in Figures 19 and 20. The measurements in Figure 19 shows the absolute reflectance measured with a so-called WV-configuration [4] for the visible spectral range and NIR region. The values can not be compared straightforward with those from measurements of the 3-layer structure in Figure 15 due to the use of different measurement set-ups. See also Discussion and conclusions concerning the difference between these samples (5-layer1 and 5-layer2). Comparing the 5-layer1 sample with Figures 9 and 10, we conclude that results from measurements and calculations are similar.

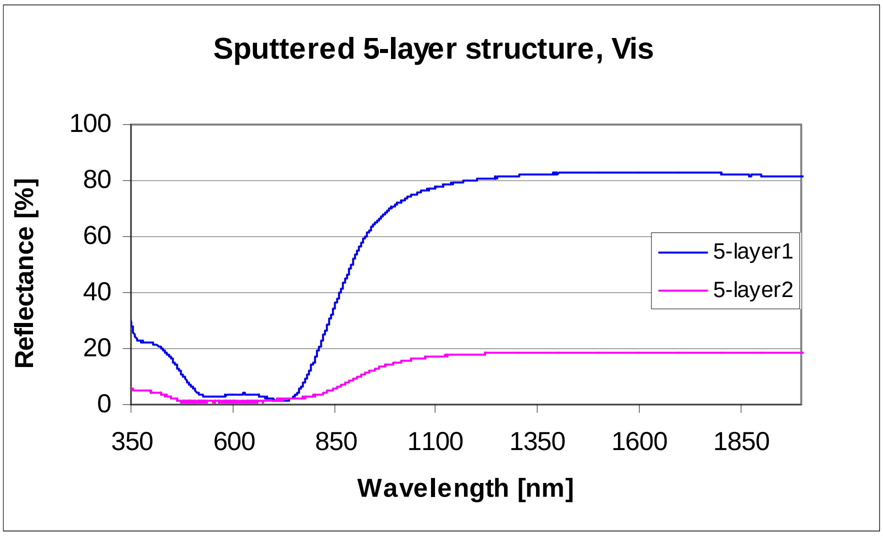

Figure 19 Sputtered 5-layer film, visible and NIR range.

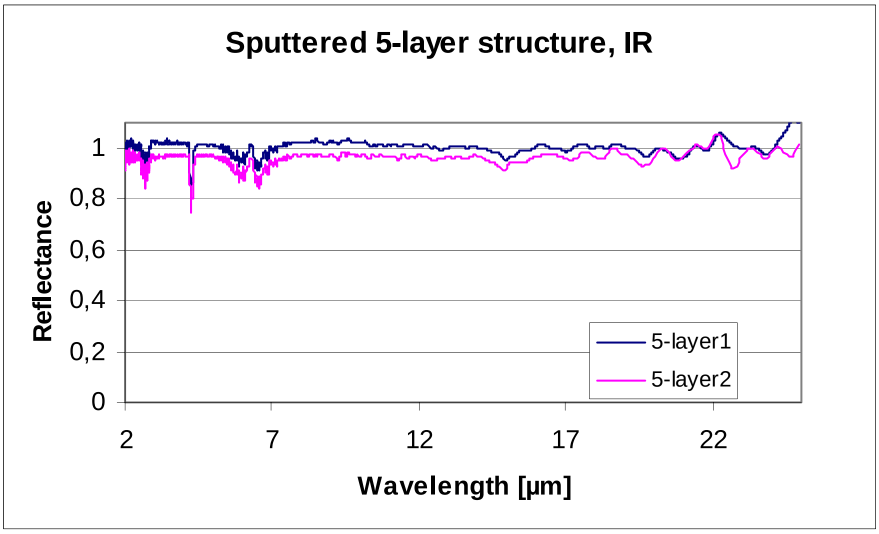

Figure 20 Sputtered 5-layer film, IR-range.

Measurements on pigment made from 5-layer films

The 5-layer coating was removed from the substrate in the same way as for the 3-layer coating. The flakes attained were piled together and spread out by diffusion by adding a drop of alcohol. The pigment flakes did not organise themselves in a complete surface coverage. The pigment from one substrate was green/blue and from the other one blue (see Figures 21 and 22).

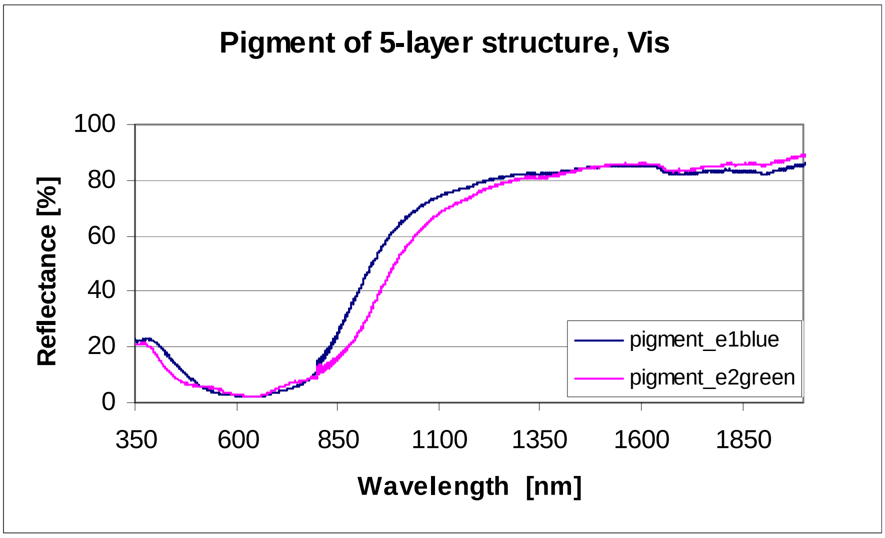

Figure 21
Pigment of 5-layer film, visible and NIR range.

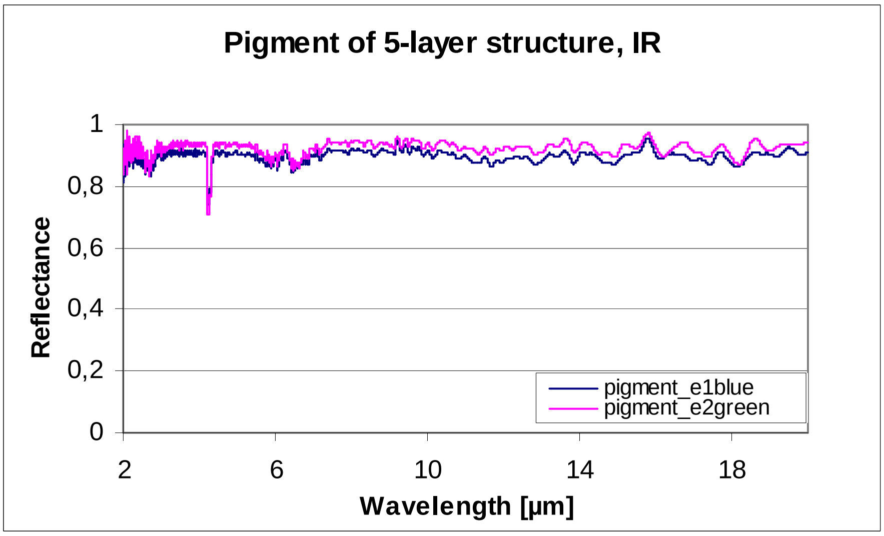

Figure 22
Pigment of 5-layer film, IR-range.

5. Measurements of paint

About 0.3g of flakes of the 3-layer structure was mixed with a commercial polymer binder called Acronal A706, which was obtained from BASF by our collaborators at DFRIT in Finland. The transmittance of the binder is found in Figure 23.

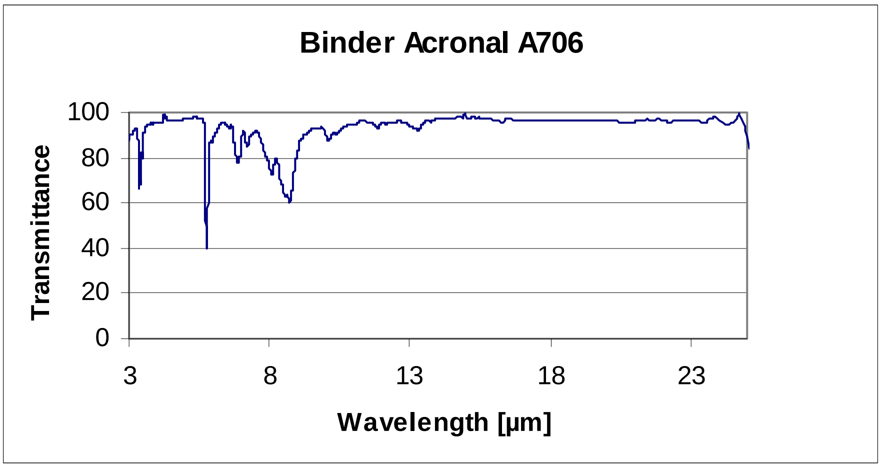

Figure 23
The transmittance of the binder Acronal A706 used for the paint.

According to absorption measurements the binder showed some weaker absorption features in the 3-3.5µm region and some broader bands around 8-9µm, which may increase the emissivity of the final paint in the atmospheric transmission regions. The transmission of the ideal binder material should be as high as possible in order not to influence the properties of the pigment [5]. A paint with flakes of the 3-layer structure used as a pigment was applied on a metal substrate. The emissivity of the paint was measured with an IR-spectrometer. The paint sample was mounted on a water container with the sample in direct contact with the water. The temperature of the water was maintained at a constant elevated temperature. The emissivity of the sample was calculated by comparing the radiance of the sample with that of a blackbody radiator, integrated in the water container. The measurement setup is similar to that described in [6]. The result of the emissivity measurement of the paint is shown in Figure 23.
However, compared to results obtained by DFRIT a lower emissivity by up to 0.35 units was achieved by using a certain grade of Al-pigment. Their results indicate suitable IR properties of this binder when matched with the proper pigment.

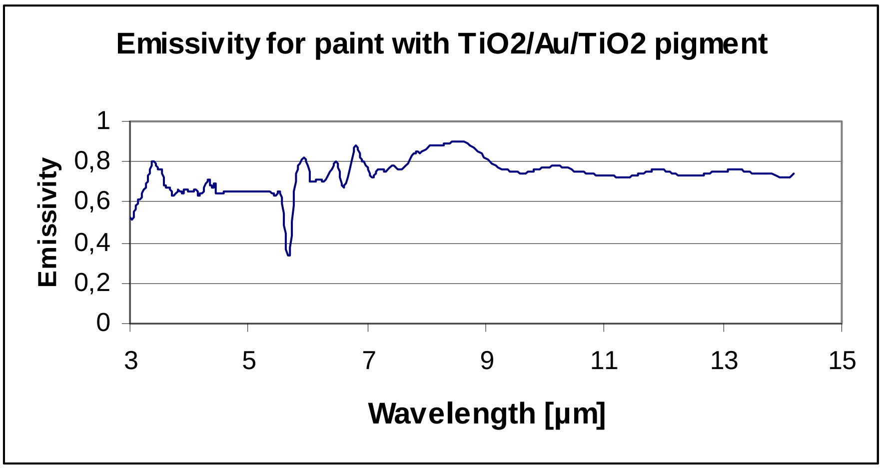

Figure 24
Emissivity measurement of a paint with flakes of the 3-layer structure used as a pigment.

6. Measurement uncertainties

The purpose of this study is to test a multilayer pigment for a low emissive camouflage paint and to get a depiction of the possibilities for the future work. Hence, since this was a study to establish the concept qualitatively, a rigorous measurement uncertainty analysis was deemed not necessary. However, the uncertainty of measured data is not believed to be the limiting factor in judging the correlation between theory and experimental results. As it stands, the restrictive factor is the reproducibility of the film itself. This is, however, a technical problem that can be overcome with fine-tuning of the process.

Most important for obtaining the same reflection properties for a sputtered multi-layered structure as compared to a modeled structure, the sputtered thicknesses have to be strictly controlled. The thickness of the sputtered layers was controlled by first measuring the thicknesses of a few different reference films, composed under different conditions, with known process parameter settings. The measurement instrument used had a resolution of 20Å. The settings of the process giving the desired thickness was then used to achieve the same thickness in the subsequent film depositions. The pressure and time constants were kept as constant as possible. Due to the fact that the sputtering equipment was not fully controlable, substrates coated during the same down-pumping session unfortunately did not attain the same coating feature.

The reflectance spectra were measured in a relative manner, eliminating the influence of instrument sensitivity.

The average size of the particles observed in a microscope was roughly 30µm. According to ref. 5, spherical pigment particles of size 20-50µm are preferred in order to obtain optimal reflection properties. There is no known method to receive a constant flake size.

7. Discussion and conclusions

The measurement results show that the reflectances of the sputtered multilayer films in general have the properties we were aiming for, i.e. they correspond to the results of the modeled structures. However, when flakes are mixed with a binder the results are not quite as satisfactory, since the high reflectance obtained for film and flakes does not result in an emissivity of the paint that is low enough (about 0.4 expected from Figure 18, 0.65-0.75 was attained).

There is therefore a need for a deeper understanding of the interaction between the binder and the pigment in order to understand and to improve the resulting emissivity of the paint. In the modeling of the layers, it was assumed that air and glass would be the boundary layers. Better results could be achieved if the refractive index of the binder is used as boundary layers of the multilayer structure in the modeling. Hence, the index of reflection of the binder must be acquired (not available at the moment) and the effects of the binder taken into account already in the modeling stage.

The size of the pigment flakes turned out to be difficult to control, hence more skill and practice is needed. The flakes were quite fragile and might have been damaged during the mixing process and hence turned into powder. Thus, the size of the particles might not have been optimal. Larger flakes can be achieved by a thicker multi-layer structure. This is the reason why calculations were also made on 5- and 7-layer structures.

In our laboratory, the sputtering process is quite time consuming since the maximum substrate size we can use is 8x5cm. In order to achieve the minimum amount of pigment needed to produce an analysable amount of paint, the process needs to be faster. As previously mentioned, a special target holder where the substrate could be turned 180 degrees and two substrates could be coated during each loading and down-pumping session, did shorten the time-consuming loading process. However, it was not realised until late in the process that the two substrates would be affected differently by the time and heat differences in the sputtering process, i.e. the two substrate-coatings were not alike. Figures 15-16, and 19-22 show this difference.

Suggestions for further work includes other deposition methods, preferably wet chemical methods should be considered, or co-operation with industry if large amounts of multi-layers are to be produced.

When designing a camouflage material it is preferable if the compounded effect of both radar and optical low observables properties are taken into account. Hence, the IR emissivity measurements should be completed by characterizations in the radar energy range.
There are other factors to be considered when developing a low emissivity paint; for example the suns reflectance below 4µm. Solar reflections on low emissive (i.e. highly reflective) surfaces may affect the signature from the object and decamouflage it. A low reflectance in the visible range is preferable, up to 4µm, where it should have ahas a steep slope to a high reflectance for the rest of the IR-region.

8. Reference

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