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FORMULATING INFRARED COATINGS FOR DEFENCE APPLICATIONS

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Abstract

Relevant physical laws governing the response of coatings to solar and infrared radiation have been reviewed. The reflection of infrared radiation by a paint is controlled primarily by the refractive index and particle size of the pigments in the coating. Pigments have been evaluated for reflectance, transparence and hiding power in the near infrared region, and guidelines for pigment selection for various applications given in terms of their optical properties in the near infrared region. Raw materials selection, manufacture and evaluation of coatings have been discussed with respect to tailoring infrared reflectance. By employing the principles developed herein and using pigments with appropriate properties, organic coatings have been developed which are consistent with the visible colour requirements of the Australian and US Navies. Significant increases in the reflection of infrared radiation have been demonstrated by the new formulations. The need for a very clear understanding of the threat systems and the operational conditions of service platforms has been emphasised. It is only with this understanding that optimum paint schemes can be devised. However, it can be stated that the use of the solar infrared reflecting paints described herein would reduce conspicuity of isolated platforms to surveillance and seeker systems operating in the mid and far infrared without detriment to visual camouflage characteristics.

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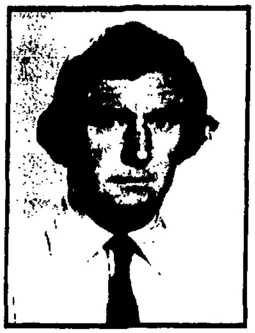

Lindsay Vernon Wake was awarded a Department of Supply scholarship to complete a PhD at the University of NSW in 1969. He joined MRL in 1972 and was briefly associated with the Textiles Group and later the Marine Environment Group of MRL. Since 1981, Dr Wake has been located in Paint Technology where he has formed a close working association with the RAAF. He is currently investigating the synthesis and performance of fire retardant paints, high temperature resistant coatings, RF and IR camouflage paints and other coating materials of Defence interest.

R.F. Brady

In 1982 Dr Brady assumed his present position as Head of the Coatings Section of the US Naval Research Laboratory. He directs and conducts basic research in polymer chemistry and coatings science. His present interests include control of volume change during polymerization, coatings based on fluorinated resins, high-solids epoxy and polyurethane coatings,, non-toxic antifouling coatings, and non-skid coatings for aircraft carriers. For one year beginning in July 1990, he was a visiting scientist at MRL, where he worked on the formulation of coatings with tailored infrared properties.

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Formulating Infrared Coatings for Defence Applications

1. Introduction

The short electromagnetic wavelengths which characterize near and thermal infrared radiation permit the use of thin coatings to control absorption and reflection of radiation in these regions. Paints can be designed which increase the reflection of incident solar radiation while retaining the visible properties of colour and gloss. The increased reflection reduces heating and lowers the energy requirements for cooling. In other instances, paints may be required to reduce the emission of thermal infrared radiation and shift infrared emissions to different wavelengths, thus reducing the likelihood of detection. Coatings may also be formulated to combine reduced emissions in the thermal region with reduced reflection in NIR bands used for laser detection.

Requirements to control infrared properties of coatings arose after the development of infrared photography. This need led to changes in paint formulation aimed at reducing reflection in the near infrared (NIR) region between 720 and 900 nm. With the increasing use of infrared detectors, paint specifications have retained the requirement for low infrared reflection. However, low NIR reflecting paints strongly absorb the NIR component of solar radiation. As such, they increase thermal infrared (TIR) signatures and the likelihood of TIR detection as well as adding to the cooling requirements. At the present time, the optimum balance for NIR or TIR signatures has received little attention.

This report examines mechanisms influencing the reflection, transmission and absorption of visible and infrared radiation by paint coatings. The report details a number of new paint formulations to meet defence coating requirements which significantly reduce thermal emissions. Consideration is also given to the selection of formulations to meet different combinations of threats and environments.

2. Physical Principles

2.1 Spectral Bands of Interest

The radiation bands of interest are the NIR region between 720 and 2500 nm, the TIR region between 2500 and 15 000 nm (2.5 and 15 mm), and the far infrared region between 15 and 50 mm.

The "photographic infrared" is traditionally regarded as the range from 700 to 950 nm, although modern infrared film is sensitive at much longer wavelengths than this range. Electronic scanning arrays are usually preferred over photographic detectors. They are used in aerial reconnaissance and cover the range from 700 to 1350 nm. Generally, the conditions under which NIR radiation emissions pose a significant threat are (i) lowlight or starlight situations where detection is usually by reflected radiation rather than by thermal emission, or (ii) by reflection of NIR laser illumination.

Two windows in the thermal infrared region, 3 to 5 mm and 8 to 14 mm are of primary importance in missile and surveillance applications because these regions are relatively free of atmospheric absorption and energy can be transmitted over moderate distances. Sensors operating in these two bands are the basis of some of the principal types of seekers in smart anti- armour munitions [1].

Some of the newer thermal detection systems also incorporate NIR targeting elements. A number of the aircraft-mounted detection systems couple forward looking thermal infrared (FLIR) sensors tailored for target detection and lock-on with a laser target designator and rangefinder operating in the NIR at 1.06 μm.

2.2 Blackbody Radiation

In addition to reflecting incident energy, coatings also radiate energy. The spectral exitance M_λ ($W.m^{-2}$) of a blackbody at wavelength λ and in a spectral range $\Delta\lambda$ is a function of temperature and is given by Planck's Radiation Formula (Equation 1) [2]

$$M_\lambda = \frac{2\pi hc^2}{\lambda^5} \cdot \frac{1}{\left(e^{hc}/k\lambda T - 1\right)} \Delta\lambda \qquad (1)$$

(in which h is Planck's constant (6.626×10^{-34} J s), c the velocity of light (2.998×10^8 m s^{-1}), k the Boltzmann constant (1.38×10^{-23} J K^{-1}), and T the absolute temperature).

The rate of energy emitted per unit area obtained from Equation 1 has been plotted for three temperatures in Figure 1. This figure shows that, with increasing temperature, the rate emitted increases markedly and the wavelength of maximum emission shifts from the TIR region toward the NIR region. Thus, it can be seen that an increase in the energy content of a body, such as that caused by the absorption of NIR radiation, results in increased emission and detectability in the 8 to 14 mm TIR region.

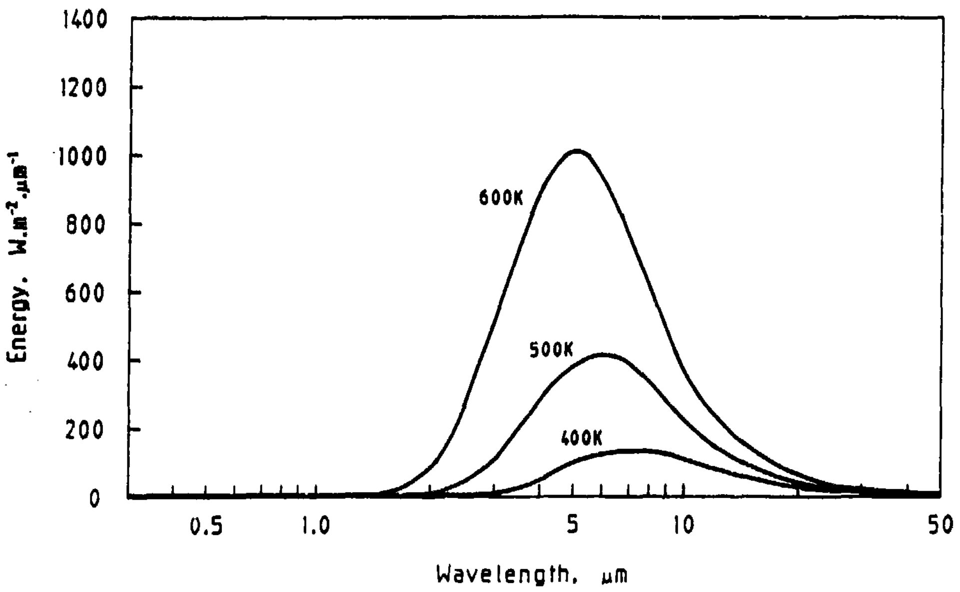

Figure 1: *Radiation energy at three temperatures.*

When Equation 1 is integrated over all wavelengths, the Stefan-Boltzmann Law (Equation 2) is obtained

$$W = \alpha T^4 \tag{2a}$$

(in which α is the Stefan-Boltzmann constant (5.67×10^{-8} W m^{-2} K^{-4}).

For non-ideal systems, the total radiative emissions are proportional to the emittance, ε, of the surface and the equation describing the total power W radiated by a body becomes

$$W = \alpha \varepsilon T^4 \tag{2b}$$

The emittance, ε, of a surface is the ratio of its emission to that of an ideal black body at the same temperature and can vary from 0 to 1. The emittance of metals such as aluminum and nickel as well as treated metal surfaces with thin oxide coatings is typically in the range from 0.05 to 0.15 and these materials are inefficient radiators of energy. As well as being poor radiators of thermal radiation, polished metal surfaces are good reflectors of incident radiation. The emittance of organic materials such as plastics and most organic coatings is high (0.85 to 0.95). When the ratio of the spectral emission of a surface to that of a black body is constant with wavelength, the surface is known as a grey body. In most cases, the emissivity varies with wavelength and the coating is said to be a selective radiator.

2.3 Solar Radiation

A specific example of a blackbody radiator is the sun. The spectral energy distribution of solar radiation at sea level with a slant path corresponding to an air mass of 1.5 [3] is shown in Figure 2. For convenience, this energy is usually divided into three bands. The ultraviolet band between 200 and 400 nm contains 5 percent of the total energy in sunlight, the visible band between 400 and 720 nm has 45 percent and the NIR band between 720 and 2500 nm contains 50 percent of the energy. Sunlight at sea level has a total intensity of approximately 1 kW m^{-2} [3]. Solar absorptance, α_s in the NIR is defined as the ratio of NIR radiation absorbed by a body to that incident upon it.

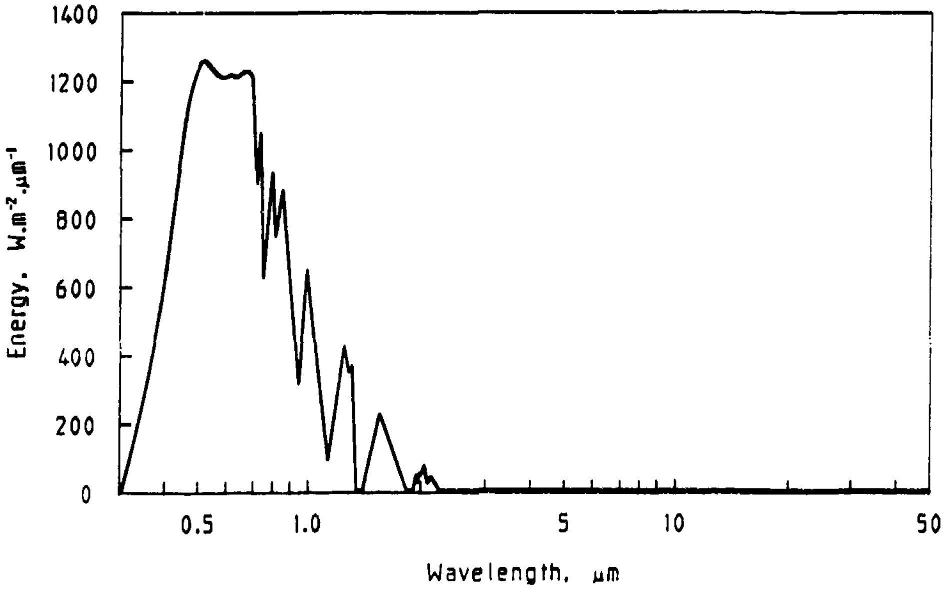

Figure 2: Spectral energy distribution of solar radiation.

2.4 Control of Infrared Properties by Coating Formulation

Incident radiation is reflected or both reflected and refracted at a coating surface. Both reflection and refraction are dependent on the refractive indices of the two media, the reflection being determined by Fresnel's Law and refraction by Snell's Law. In paint terminology, a description of the mirror-like reflection or specular reflection at the surface of the coating is termed gloss, as distinct from the reflectance of the coating which is also dependent on pigments and fillers in the coating. Specular reflection is strongly increased by leafing pigments such as metal flakes. Gloss is principally dependent on the angle of incidence and the smoothness of the surface, being high for smooth surfaces and low for irregular surfaces.

Infrared radiation entering a paint coating is refracted at the interface before encountering the pigment and filler particles. The radiation is partially reflected and partially refracted at the surfaces of these particles and in normal pigmented paints the process of multiple reflection and refraction thoroughly diffuses the beam. A proportion of this radiation propagates back to the coating surface where it leaves in all directions. Diffusion of radiation arises from a large number of essentially random scattering events and in paint technology, the overall diffusion process is simply termed "scattering".

The selection of pigments largely determines the thermal control provided by coatings. The most important aspects of these are the solar absorptance, α_s, in the NIR and the emittance, ε, in the TIR regions. Examples of specific thermal requirements include (i) high solar absorptance to reduce photographic or NIR laser detectibility, (ii) low solar absorptance to keep illuminated equipment cool in hot environments or, (iii) low emittance to reduce thermal detectability. Coatings may combine low emittance properties with either high or low levels of solar absorptance.

Camouflage of defence equipment in the visible waveband is usually achieved by the use of dark coloured low gloss paints. Dark coloured paints, e.g. navy greys, are commonly formulated with carbon black which is a strong absorber of solar radiation and reduces photographic and laser detectibility in the NIR. However, paints formulated with carbon black have high emissivities and strongly emit thermal radiation. A number of metal oxide coatings applied to metal substrates combine high solar absorption with low emissivity in the TIR as thin oxide layers absorb short wavelength radiation but are transparent in the longer wavelength infrared region. These absorption characteristics act to reduce the chance of detection in both TIR and NIR regions. However, as these coatings strongly absorb solar radiation, heat build-up may be a problem. By replacing carbon black or the black metal oxides with organic perylene blacks which absorb weakly in the NIR, paints can be formulated in the same colours to reduce solar heating. Like the metal-metal oxide paints, the perylene black paints are selective absorbers, however, whereas the metal-metal oxide paints absorb strongly in the NIR and poorly in the TIR, the perylene black coatings absorb weakly in the NIR region and strongly in the TIR region. Low emittance paints may also be formulated with metal flakes, e.g. aluminium, which provide strong reflection across the visible and infrared spectrum.

The reduced thermal exitance resulting from either lower temperatures or low emittance reduces the chances of thermal infrared detection. However, when the detector system has both near and thermal detecting elements, such as in some of the air borne systems, the requirements involved in paint selection are more complex. Under normal conditions, the laser system has greater range than the TIR detectors. This imbalance permits active rangefinding well outside passive acquisition range. The use of solar reflecting paints will accentuate the imbalance by reducing the acquisition range while further increasing the active NIR rangefinding capability. Under normal daylight conditions this will lower the detection range while having little effect at night. An alternative paint for this application would be the NIR absorbing, low emittance metal-metal oxide paints. However, their use under Australian conditions, particularly in northern Australia, would result in considerable heat build-up.

It should be appreciated from the above examples that paints may be formulated which provide either (i) absorption across the NIR and TIR regions, (ii) reflection across the NIR and TIR regions, or (iii) absorption in the NIR and reflection in the TIR region or vice versa.

2.5 *Properties of Coatings Determining Infrared Performance*

2.5.1 *Reflection of Radiation*

The specular and diffuse reflectance of infrared radiation from a coating results from reflecting and scattering processes occurring at the surface and within the coating. The reflectivity is defined as the ratio of the reflected to the incident energy. At flat surfaces, specular reflection will occur in accordance with Fresnel's Law from which the reflection coefficient (ρ) may be derived [4]:

$$\rho = \frac{(n-1)^2 + n^2\chi^2}{(n+1)^2 + n^2\chi^2} \tag{3}$$

(in which n is the ratio between the refractive indices of the two media and χ is the extinction coefficient).

From Equation 3, we see that when $n\chi$ is large (good absorbers) compared to $n + 1$, the reflecting power is nearly unity, i.e. strong reflection is associated with strong absorption. This result is in agreement with experimental observation [5]. Highly conductive materials, e.g. metals, do not allow electromagnetic propagation at optical or infrared frequencies. The electromagnetic fields are attenuated so rapidly that, at thicknesses exceeding the skin depth, the reflection coefficients are close to unity. 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 may approach unity. The small particles will also provide diffuse multiple scattering, particularly when the particle sizes approach light wavelengths. This is the basis of the action of the metallic blacks.

From Kirchhoff's Law (Equation 4), it can be seen that coatings which are good reflectors have low emissivities [6],

$$\varepsilon_\lambda = \left[1 - \rho_\lambda\right]\left[1 - e^{-4\pi\chi_\lambda l/\lambda}\right] \tag{4}$$

(where ε_λ is the emissivity, ρ_λ the fraction of the radiation reflected, $4\pi\chi_\lambda$ the absorption coefficient and l the depth). The first term in Kirchhoff's Equation, $1 - \rho_\lambda$ which is the proportion of radiant flux penetrating the body, becomes quite small for good reflectors. The second term, $1 - e^{-4\pi\chi_\lambda l/\lambda}$ is the proportion of flux penetrating the body and absorbed by it. In the infrared spectral region, even a small thickness of matter will usually absorb the entire refracted flux, so that equation 4 reduces to

$$e_\lambda = 1 - \rho_\lambda \tag{5}$$

For materials of high conductivity, the reflectance (and emittance) can be reduced to equations dependent only on conductivity [7], viz

$$\rho = 1 - 2\sqrt{\frac{4\pi.\varepsilon_0.c}{\sigma.\lambda}} \tag{6}$$

(where σ is the conductivity and c the velocity of light).

Equation 6 is in close agreement with experimental observations [5]. It is seen that the emittance of conducting materials decreases as the wavelength increases and, in practice, paints with low thermal emissivities are 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.

2.5.2 Scattering of Radiation

Scattering of visible and infrared radiation is a single stage process and is commonly referred to as being either elastic or inelastic. Scattering in which the radiation retains the same quantity of energy and momentum and hence with an unchanged frequency is considered to be elastic. Rayleigh scattering is such a process. Scattering in which the energy is exchanged with the scattering object is termed inelastic and is referred to as Raman scattering. It is much weaker than Rayleigh scattering. 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.

There are other phenomena which involve a two stage process of absorption and reradiation of the energy after a delay. These are termed luminescence, fluorescence or phosphorescence, depending on the delay time, however they are not considered to be scattering.

Elastic and inelastic scattering processes result from electromagnetic radiation perturbing the electronic cloud surrounding the molecules of the irradiated material. Weakly bound electrons are most able to respond to the fields of the radiation with increased delays at higher frequencies. The electrons attempt to screen the alternating electric field of the incoming beam. This field can induce an energy transition in the material with a corresponding energy change of the infrared photon. Inelastic scattering of this kind is called the Raman effect in condensed media.

Rayleigh scattering occurs in the presence of small independent particles commonly present in colloidal and other suspensions containing particles with sizes comparable to or larger than the wavelengths involved. Such scattering, which is nearly wavelength independent, is called "white scattering" and is also known as the Tindall Effect. Rayleigh scattering has been extended by other authors to particles of any size provided that the refractive index is nearly unity. As Scott [8] has pointed out, a more complete theory was developed earlier by Mie which covers the deficiencies in Rayleigh Theory.

The scattering of visible and infrared radiation by a pigment is a function of the refractive indices of the pigment and the resin in which it is dispersed. The refractive index of commercial pigments varies between 1.4 and 2.8. The scattering power *m* of a pigment for white light is calculated by dividing the refractive index of the pigment by that of the resin. Hiding pigments have values of *m* well above 1; they hide the substrate and modify the reflectance curve of the coating. Red iron oxide and titanium dioxide, which are among the most effective hiding pigments, have *m* values of 1.9. Extender pigments, i.e. achromatic pigments of low refractive index, such as barytes, talc, and silica have values of *m* below 1.1; they scatter light poorly, do not alter the shape of the reflectance curve but do modify the reflectivity.

Substantial changes in scattering power cannot be achieved by the choice of resin because conventional paint resins do not show a large variation in refractive index. Common organic resins have refractive indices between 1.45 and 1.50 and conventional alkyd and epoxy resins have refractive indices near 1.48. Fluoropolymers possess comparatively low refractive indices [9] in the range of 1.34 to 1.42 and fluoropolymer coatings made with titanium dioxide [10] scatter light very effectively because of the large value of m.

For a fixed value of the scattering power m, the wavelength most efficiently scattered by a particle of diameter d is given by Equation 7 [11],

$$\lambda = \frac{d}{\kappa} \tag{7}$$

in which

$$\kappa = \frac{0.90\left(m^2 + 2\right)}{n\pi\left(m^2 - 1\right)} \tag{8}$$

In Equation 8, n is the refractive index of the resin in the paint. Table 1 contains values of n, m and κ for common paint pigments dispersed in an alkyd resin having a refractive index of 1.48. In a later study using the Mie scattering theory it was shown that, to a good approximation, the same relationship may be extended to different wavelengths with correspondingly different optimum particle sizes [12].

Commercial titanium dioxide pigments are manufactured with a particle size of 200 nm, the optimum value for scattering visible radiation with a peak intensity of 500 nm [13]. As can be seen in Equations 7 and 8, larger particle sizes will be required to scatter the longer wavelengths of infrared radiation. For titanium dioxide and red iron oxide, 1 mm particles would effectively scatter near infrared radiation at 2.3 mm, but for other pigments, larger particle sizes would be needed to scatter light at the same wavelength. To scatter thermal infrared radiation, particles several micrometers in diameter would be required.

2.5.3 Absorption of Radiation

The coefficient of absorption of radiation will, in general, vary with wavelength. When radiation passes through a gas, certain wavelengths are preferentially absorbed. These are the same as those observed in the emission spectrum of the gas. In homogeneous condensed materials, molecular interactions broaden the electronic states.

Infrared radiation incident upon a paint may cause polarization of the electrical and magnetic (polar) components within the compounds which comprise the paint. Alignment of permanent dipoles is ineffective at high frequencies (infrared frequencies) because the movement of dipoles is too slow to follow field variation [4]. The external electric field component reacts with the electric field of the atom or molecule displacing the electrons relative to the nucleus. Spectra observed in the infrared are mostly due to transitions between the energy levels of molecules rather than atoms. Strong absorption of infrared radiation occurs only for transitions between states with different dipole moments. Thus there are no infrared spectral absorptions from symmetric molecules, e.g. nitrogen and oxygen. Water vapour and carbon dioxide, on the other hand, are responsible for most of the absorption of radiant energy by the earth's atmosphere.

Table 1: *Constants used to calculate the scattering power of pigments*

Pigment	Refractive Index	Scattering Power[a] (m)	κ
Diatomaceous silica	1.43	0.97	-
Amorphous silica	1.55	1.05	5.86
Magnesium silicate	1.58	1.07	4.20
Barium sulfate	1.64	1.11	2.70
Chromium oxide	1.90	1.28	1.10
Zirconium dioxide	2.20	1.49	0.67
Yellow iron oxide	2.30	1.89	0.42
Red iron oxide	2.80	1.89	0.42
Titanium dioxide	2.81	1.90	0.42

[a] In an alkyd resin having a refractive index of 1.48.

3. *Raw Materials*

3.1 Measurement of Near Infrared Properties of Pigments

Pigments exert the principal influence on the optical and NIR properties of coatings [14]. Pigments used in infrared coatings are chosen because of their diffuse and specular reflectance, absorptance and transparence in the infrared region. A knowledge of the behavior of pigments in the infrared region is a critical factor in formulating coatings to specific requirements. The particular pigments required will depend on the intended application.

Compilations of absorption spectra of prime pigments, i.e. pigments possessing good hiding power, and of extender pigments are available for the thermal [15, 16] and far [17] infrared regions. They provide information about the position and intensity of absorption bands. Most published measurements, which have been made on pressed pure pigments in powder or tablet form, give no information on the refractive index nor of pigment-volume concentration (PVC). Preparation of a pigment for measurement of its spectrum may reduce its particle size; absorption would not be modified but scattering would be influenced as discussed in paragraph 2.5.2. In addition, dispersion of a pigment in an alkali metal halide matrix, a common sample handling technique for obtaining infrared absorption spectra, creates refractive index differences which are not found in paint films. Thus they are of little use in the design or prediction of NIR reflection of paint films.

The concepts of scattering and opacity are useful throughout the infrared spectrum as well as the visible spectrum. The combination of diffuse reflection and selective absorption of light by pigments determines the hiding power of the paint, that is, its ability to screen the substrate from incident light energy. Measurement of scattering of infrared radiation at 2.5 µm is a useful method to evaluate pigment dispersion [18].

Hiding power and reflectance are characteristics of a paint film rather than of a pigment. The behaviour of a pure pigment will change when it is incorporated into a paint. For example, non-absorbing pigment particles which reflect as pressed powders allow considerable transmission of infrared radiation when incorporated into paint films at conventional pigment volume concentrations [19].

A representative group of pigments was selected for the present study of their infrared properties. In view of the large differences in oil (resin) absorption by pigments in paint films, each pigment was dispersed in a standard resin at the same percentage of its critical pigment volume concentration (CPVC) [20] rather than at a fixed concentration. (The CPVC is the level of pigmentation, i.e PVC, where just sufficient binder is present to fill the voids between the pigment particles. Sharp changes in film properties occur at this point.) An approximate value for the CPVC, which makes allowance for oil absorption, was calculated by Equation 9 [21]

$$\mathrm{CPVC} = \frac{1}{1 + \dfrac{SG_p \times OA_p}{SG_r \times 100}} \tag{9}$$

in which SG_p and SG_r represent the specific gravity of the pigment and resin, respectively, and OA_p is the oil absorption of the pigment in grams of oil per 100 grams of pigment. In order to produce the semi-gloss finish of most camouflage coatings, the pigments were dispersed in a resin to produce a paint having PVC/CPVC = 0.5, a value characteristic of semigloss paints [22] but this value may be adjusted depending on the intended application. Total paint solids, i.e. pigment plus binder, were adjusted to 50 percent by volume, and drawdowns with a 125 µm blade produced dry films 75 to 88 µm thick.

A spectrophotometer operating in the visible and infrared regions and equipped with an integrating sphere was used to measure the diffuse reflectance spectra of the dry films over the wavelength range 400-2300 nm. Measurements of diffuse infrared reflectance are made over highly reflecting white (R_w) and highly absorbing black (R_b) surfaces. Data obtained with a Cary Model 2300 recording spectrophotometer for some representative pigments are given in Table 2.

The infrared properties of pigments can also be estimated simply and rapidly by measuring their infrared reflectance in a narrow NIR band. This technique is useful and convenient, but gives much less information than measurement of the diffuse reflectance spectrum. An EEL Reflectometer (Evans Electroselenium Ltd., Essex, U.K.) modified with cadmium sulfide detectors and Wratten 88A filters was used for measurements [23]. The sensitivity of this instrument starts from zero at 730 nm, rises fairly sharply to a peak response at about 770 nm, and then decreases steadily to zero at about 890 nm [24]. Data from this technique are given in Table 3, and compare favorably with the spectrophotometric data in Table 2. Using films 75 to 88 µm thick, the contrast ratio (CR_{IR}) at 800 nm in the infrared was calculated for each pigment using Equation 10 and is also given in Table 3.

Table 2: Diffuse reflectance values (in percent) of paint films applied over white (R_w) and black (R_b) backgrounds.[a,b]

Pigment		Wavelength (nm)									
		400	500	600	700	800	900	1000	1100	1200	1300
Barytes	R_w	56	81	88	90	90	88	88	88	84	84
	R_b	5	5	5	5	0	0	5	5	2	0
Carbazole Dioxazine Violet	R_w	3	3	3	7	25	40	62	75	75	80
	R_b	3	3	3	7	7					
Chromium Oxide	R_w	11	9	8	18	50	47	40	42	42	38
	R_b	11	9	8	18	50	47	40	42	42	38
Heliogen Black	R_w	4	4	4	5	50	80	85	88	84	88
	R_b	4	4	4	5	6	9	21	29	30	28
Iron Oxide, Red	R_w	2	2	14	28	25	12	30	45	42	37
	R_b	2	2	14	28	25	12	35	45	42	37
Iron Oxide, Yellow	R_w	3	7	37	35	37	24	22	38	65	73
	R_b	3	7	37	35	37	12	20	29	27	22
Iron Oxide, Lt. Brown	R_w	6	7	16	18	17	13	11	7	4	1
	R_b	6	7	16	18	17	13	11	7	4	1
Iron Oxide, D. Brown	R_w	3	3	4	4	4	4	0	0	0	0
	R_b	3	3	4	4	4	4	0	0	0	0
Iron Oxide, Black	R_w	5	5	5	5	0	0	0	0	0	0
	R_b	5	5	5	5	0	0	0	0	0	0
Paliogen Black	R_w	3	3	3	25	67	67	67	66	64	64
	R_b	3	3	3	10	10	8	4	4	4	4
Silica Amorphous, 25 µm	R_w	62	81	86	90	89	88	87	87	85	85
	R_b	5	5	6	6	3	3	4	5	4	3
Silica Amorphous, 22 µm	R_w	51	73	78	82	94	92	89	87	85	85
	R_b	5	5	5	5	4	4	4	3	2	1
Silica Amorphous, 16 µm	R_w	60	81	86	90	92	92	90	88	83	85
	R_b	5	5	5	5	5	1	3	3	0	0
Silica, Diatomaceous	R_w	57	83	89	91	97	94	94	94	90	90
	R_b	6	6	6	6	0	0	0	0	4	8
Talc	R_w	39	53	53	53	92	92	91	90	87	87
	R_b	6	9	10	11	2	0	0	0	0	0
Titanium Dioxide, 0.2 µm	R_w	30	94	94	94	94	92	89	87	85	85
	R_b	30	94	92	88	84	75	70	64	58	53
Titanium Dioxide, 10 µm	R_w	10	67	71	75	83	84	85	86	85	86
	R_b	10	42	41	39	31	29	27	25	23	23
White Background	R_w	72	84	88	90	92	90	89	89	86	86
Black Background	R_w	0	0	0	0	2	3	4	5	5	5

[a] Measurements are relative to a pressed white poly(tetrafluoroethylene) powder which was assigned a value of 100%.

[b] Changes in filters and detectors at 800 nm produced a discontinuous baseline at that point.

Table 2 (Contd): Diffuse reflectance values (in percent) of paint films applied over white (R_w) and black (R_b) backgrounds.[a,b]

Pigment		Wavelength (nm)									
		1400	1500	1600	1700	1800	1900	2000	2100	2200	2300
Barytes	R_w	73	67	71	70	70	64	61	44	46	33
	R_b	0	0	5	9	11	9	5	0	0	0
Carbazole Dioxazine Violet	R_w	71	78	71	63	66	55	57	44	48	30
	R_b										
Chromium Oxide	R_w	37	37	37	32	35	43	43	37	34	26
	R_b	35	33	31	31	35	39	35	28	27	26
Heliogen Black	R_w	76	68	73	68	70	62	59	39	41	25
	R_b										
Iron Oxide, Red	R_w	44	39	41	40	42	38	34	28	34	28
	R_b	44	39	41	32	35	38	34	28	34	28
Iron Oxide, Yellow	R_w	68	32	32	54	59	54	54	37	39	26
	R_b	12	12	15	14	7	2	2	10	9	2
Iron Oxide, Lt. Brown	R_w	0	0	0	0	2	4	5	7	6	5
	R_b	0	0	0	0	2	4	5	7	6	5
Iron Oxide, D. Brown	R_w	0	0	0	0	0	0	0	0	1	1
	R_b	0	0	0	0	0	0	0	0	1	1
Iron Oxide, Black	R_w	0	[illegible]	0	0	[illegible]	1	1	1	1	0
	R_b	0	0	0	0	0	0	0	0	0	0
Paliogen Black	R_w	64	53	49	53	53	53	46	33	35	33
	R_b	2	2	2	4	7	9	14	14	17	13
Silica Amorphous, 25 µm	R_w	72	67	70	72	72	70	65	50	53	45
	R_b	1	0	0	0	0	1	5	7	10	9
Silica Amorphous, 22 µm	R_w	73	70	71	67	70	55	55	45	45	30
	R_b	0	0	0	0	0	0	6	7	11	11
Silica Amorphous, 16 µm	R_w	72	68	70	67	71	64	63	44	44	24
	R_b	0	2	7	4	0	0	0	3	10	4
Silica, Diatomaceous	R_w	76	72	75	72	73	65	64	47	50	30
	R_b	9	8	4	2	1	2	8	11	13	8
Talc	R_w	79	70	72	72	72	68	63	47	47	30
	R_b	0	0	0	0	0	4	10	12	14	15
Titanium Dioxide, 0.2 µm	R_w	73	70	70	63	63	55	55	45	45	30
	R_b	47	43	38	32	30	27	23	18	14	10
Titanium Dioxide, 10 µm	R_w	80	71	72	72	72	68	64	57	60	44
	R_b	23	23	24	24	25	30	30	30	30	28
White Background	R_w	80	70	72	75	74	72	67	55	52	50
Black Background	R_w	7	7	8	9	9	10	10	10	10	10

[a] Measurements are relative to a pressed white poly(tetrafluoroethylene) powder which was assigned a value of 100%.

[b] Changes in filters and detectors at 800 nm produced a discontinuous baseline at that point.

Table 3: Near infrared (730 to 890 nm) reflectance data for pigments

Pigment	R_w	R_b	CR_{ir}
Barytes	99	1	1
Carbazole dioxazine violet	26	3	11
Chromium oxide	45	44	99
Heliogen black	52	6	13
Paliogen black	73	9	12
Iron oxide, red	33	33	100
Iron oxide, yellow	56	56	100
Iron oxide, lt brown	16	16	100
Iron oxide, dk brown	0	0	100
Iron oxide, black	0	0	100
Silica, amorphous, 25µm	95	1	1
Silica, amorphous, 22 µm	96	2	2
Silica, amorphous, 16 µm	95	2	2
Silica, diatomaceous	99	2	2
Talc	96	1	1
Titanium Dioxide, 0.2 µm	100	93	93
Titanium Dioxide, 10 µm	91	40	44
White card	99		
Black card	1		

$$CR_{ir} = \frac{R_{black} \times 100}{R_{white}} \qquad (10)$$

By means of these measurements, each pigment was classified according to its reflectance and contrast ratio into one of six categories as shown in Table 4. Each pigment was found to be either highly reflective, highly absorbent, transparent, or intermediate in behavior between any two of these categories. When R_W greatly exceeds R_B, the pigment is transparent and has little or no hiding power, but similar values of R_W and R_B denote high contrast ratios. Values of R_W and R_B which are similar and high indicate that hiding is principally achieved by diffuse reflectance, whereas values which are similar and low indicate that hiding is caused by absorption; in both of these cases the contrast ratio is high, usually above 0.90.

3.2 Selecting Pigments for Applications in the Near Infrared

A wide variety of useful NIR properties are obtained when pigments are dispersed in films. Titanium dioxide pigments reflect NIR radiation very well, as indicated by their high value of *m*. Different particle sizes have optimum reflectances in different parts of the spectrum, as shown in Equations 7 and 8. Conventional titanium dioxide with a mean particle size of 200 nm reflects well between 400 and 1700 nm, and is used where reflectance in the visible region is most important.

Table 4: Infrared properties of pigments

R_w

Transparent		Reflective		Highly Reflective	
R_b	0.2	R_b	15-60	R_b	87-100
R_W	87-100	R_W	87-100	R_W	87-100
CR_{IR}	0.2	CR_{IR}	15-60	CR_{IR}	87-100
e.g. Amorphous SiO_2		e.g. TiO_2	10 µm	e.g. TiO_2	0.2 µm

Absorbent-Transparent		Reflective-Transparent	
R_b	3-10	R_b	15-60
R_W	25-75	R_W	15-60
CR_{IR}	0.2	R_W	87-100
e.g. Paliogen Black		e.g. Chromium Oxide	

Highly Absorbent	
R_b	0-2
R_W	0-2
CR_{IR}	87-100
e.g. Black Iron Oxide	

R_b

Titanium dioxide with a mean particle size of 10 µm reflects efficiently between 800 and 2300 nm but rather poorly in the visible spectrum between 400 and 800 nm. This pigment behaves as an extender in the visible with high reflectance in the infrared. It has little or no effect on the visual colour of the coating and can be substituted for other extenders to produce non-metameric (i.e., matching which is independent of spectral irradiance) colours with enhanced infrared reflectance.

Chromium trioxide and the iron oxides are moderate to strong absorbers of NIR radiation. They are valuable hiding pigments, but only enough should be used in infrared reflective coatings to achieve the desired visual hiding; excessive absorption will result if larger amounts are used.

Pigments which absorb in the visible region (required for visual coloration) but are transparent in the NIR can be considered to be extenders so far as NIR radiation is concerned; that is, they can be used to modify the visual appearance of the paint without affecting its infrared properties. Organic pigments such as the perylene blacks, phthalocyanine blues and greens, and carbazole dioxazine violet are useful for this purpose.

Conventional extender pigments such as barytes, amorphous and diatomaceous silica, and talc are transparent and nonreflective throughout the visible and NIR regions. These pigments are valuable where transparency in the NIR is needed, and they do not interfere with the performance of other pigments.

Carbon black absorbs strongly throughout the NIR and TIR regions [19]. When used in small amounts it is effective in decreasing the level of infrared reflectance without greatly affecting visible colour. However, should the required reflectance of the paint in the NIR or TIR be low, the amount of carbon black necessary to bring the reflectance down to this level will have a substantial effect on the visual appearance of the paint.

In addition to spectral factors, conventional coating considerations also play a part in the selection of pigments. These include can-stability, resistance to formation of a friable powder on the surface on exposure (chalking), resistance of flat coatings to polishing to a higher gloss (burnishing), and durability. In modern high solids coatings, pigments having the lowest possible product of oil absorption and specific gravity are valued, as they require less resin and are relatively free of settling problems.

3.3 Selecting Pigments for Applications in the Thermal Infrared

The technique of using large pigment particles to promote scattering is restricted in the TIR region. For example, in order to scatter radiation at 12 μm, titanium dioxide particles 5 μm in diameter are required, and particles of this size, i.e. Hegman 7.5, (the Hegman scale is a measure of the fineness of dispersion of a pigment, larger numbers indicating larger particles) are large enough to affect the gloss of a coating. If radiation at 12 μm is to be effectively scattered by a pigment with a low value of m, such as talc, a 50 μm-particle would be required. A particle 50 μm in diameter, i.e. Hegman 4, is the largest that could be tolerated; it would make a coating visibly coarse and would affect colour uniformity, dirt retention, and other important performance properties [25].

In addition, most inorganic pigments have strong, broad absorption bands in the TIR region. For example, carbonates absorb near 7 μm, silicates around 9 μm, and oxides between 9 μm and 30 μm. Organic pigments such as the perylene blacks, phthalocyanine blues and greens, and carbazole dioxazine violet show strong, sharp absorption bands throughout the TIR region, but principally between 6 and 11 μm. Thus, properties of coatings will be influenced by the pigments used and will be strongly wavelength dependent, and grey body approximations are likely to lead to considerable error.

For this reason, metallic pigments, particularly metal flake pigments, are preferred in the TIR region. They absorb TIR energy poorly, but scatter and reflect efficiently throughout this region. Hagen-Rubens [26] first attributed the high infrared reflectance of metals as being due to their high density of conduction electrons. Coatings filled with metallic pigments, particularly leafing pigments, do not demonstrate appreciable wavelength dependence, and so grey-body approximations can be used.

3.4 *Spectral Properties of Resins*

There are two principal requirements for resins in tailored infrared coatings. First, the resin must protect the pigments and preserve their infrared properties throughout the service life of the coating. In addition, the resin must be sufficiently transparent in the spectral region of interest.

Most organic resins are free from strong absorptions in the NIR region and can be used for many applications in this part of the spectrum.

However, in contrast to the characteristics of paints in the visible and NIR regions, paint behaviour in the TIR region is strongly influenced by the resin, and the performance of the coating is determined by the nature of both the pigment and the resin. Organic resins 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 mm (C-O stretch) are usually prominent. A collection [15] of infrared absorption spectra of organic resins is a useful aid in selecting a resin.

Strong absorption in the TIR can be avoided by choosing resins 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 [27]. 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 [28]. Inorganic silicate oligomers form polymers which contain only silicon-oxygen bonds [29], these resins show low emittance except for a band near 9 µm.

Absorption by resins can also be diminished by the selection of pigments which, because of their refractive indices and particle sizes, scatter light effectively in bands where resins absorb. This technique can be used to great advantage in the TIR region. In addition, leafing metallic pigments which form a practically continuous film reduce the penetration of incident radiation and absorption by the underlying resin.

4. *Formulation*

4.1 *Preparing for Formulation*

Before beginning the formulation of any coating with specified infrared properties, the illuminants and conditions of illumination, the spectral response of the detector or viewer, the desired visual colour of the coating, and the spectral distribution of the radiation to be reflected or absorbed must be defined. The next step is to select a vehicle with good heat resistance and minimal absorption in the infrared bands of interest. Pigments are then selected and, the refractive index of the resin being known, the required particle size distribution is calculated using Equations 7 and 8. Special attention must be given to bands where the resin absorbs strongly and to the regions where reflection of infrared radiation is especially desired.

4.2 *Control of Colour*

The colour of a coating (i.e., its visible reflectance spectrum) is normally established for cosmetic or camouflage requirements, and the opportunity to alter the amount of visible light reflected or its wavelength distribution is severely restricted. Two avenues of approach to colour matching are available. First, a pigment which is transparent in the visible region but highly reflective in the infrared can raise the infrared reflectance without affecting the visible colour, and a nonmetameric match to the desired colour can be made. An example of an appropriate pigment for this is the large particle size titanium dioxide discussed in paragraph 3.2.

Alternatively, pigments employed for visual colour match which absorb strongly in the infrared can be removed and replaced with pigments which show similar absorptions in the visible but reflect or are transparent in the infrared. This is seldom a simple matter, and additional pigments will have to be added to duplicate the desired colour. As an example, carbon black can be replaced by an organic perylene black such as Paliogen Black [30] or Heliogen Black [31]. When used as tints, the former has a green shade and the latter has a violet shade. A colorant such as red or yellow iron oxide, respectively, must be added to re-establish a true black or grey shade. The colour thus produced will be metameric to the original colour, and the old and new colours may not match under all types of illumination or observation.

Where reflectance is important, the amount of hiding pigments which absorb should be just sufficient to meet the requirements for hiding. The balance of the pigmentation should be made up of extender pigments with optimized infrared reflectance.

4.3 *Control of Emissivity in the Thermal Infrared*

The emissivity of a coating contributes directly to its signature in the TIR region, and emissivity as well as reflectance must be controlled in order to achieve the performance desired. Organic resins are strong emitters in the thermal infrared region, particularly at the wavelengths which are found in their absorption spectra. Oxide, carbonate, and silicate pigments show selective emission; for example, titanium dioxide emits near 8 µm.

Finely dispersed metallic pigments such as aluminum flake have low emissivity and are used to decrease the emissivity of organic coatings. Bright aluminum foil has a reflectance of about 95 percent for black body radiation from a source at 50°C; the maximum energy from such a source is emitted at 9 µm. Aluminum paints show reflectivity as high as 82 percent and emissivity as low as 18 percent [32].

Clean or polished metallic substrates radiate heat poorly, but their emissivity can be enhanced by a wide range of black or dark oxide, phosphate, chromate and other coatings applied by chemical or electrochemical processes [33]. When cooling of a coated object is important, high emissivity coatings are used. On the other hand, coatings with low emissivity are used to retain heat within, for example, steam pipes or boilers.

5. *Coatings with Tailored Infrared Reflectance*

5.1 Low NIR or Low TIR Signature?

Defence equipment used by Australian and overseas forces is painted in a range of schemes which are designed to absorb and/or reflect in the infrared region. In part, selection of the infrared characteristics is determined by the operational role of the equipment. The Australian Army's Disruptive Pattern Paint scheme used for camouflage employs three paints which have relatively low NIR reflecting values, each differing from the other to create a disruptive pattern in the NIR as well as in the visible. This scheme is designed to protect against systems (considered to be major threats) which use the NIR waveband and operate in low light conditions.

The painting practices for military aircraft suggest that the detection threat has not been clearly identified for the environmental conditions in which they operate. Where solar radiation is low, as in a number of NATO countries, solar heating and the consequent increase in TIR signature will be of little importance. However, in subtropical and tropical countries, low NIR reflecting paints result in excessive heat loads and significantly higher TIR signatures, particularly in the 8 to 14 µm region. As the threat to aircraft by NIR photographic detection is minimal and there are no anti-aircraft missiles using the NIR waveband, the advantage provided by these paints would seem to be outweighed by their disadvantages.

A number of military aircraft are painted in highly reflecting NIR paints and others in highly absorbing NIR paints. However, some local and overseas military aircraft are painted with highly absorbing NIR primers but employ highly reflecting NIR topcoats, a practice that is counterproductive. An understanding is required that the term low infrared reflecting paint generally means a paint that is highly absorbing in the NIR (with a consequently higher TIR signature on exposure to sunlight). Likewise, the term high infrared reflecting paint refers to highly reflecting NIR paint (with a consequently lower TIR signature on exposure to sunlight).

5.2 Solar Heat (near infrared) Reflecting Coatings

Coatings formulated to reflect a high proportion of solar radiation lower the absorption of solar energy and the consequent temperature of the surface.

Absorptance in the ultraviolet region contributes little to the total energy absorbed by a coating, and it is usually not profitable to direct attention to this portion of the spectrum. The visible reflectance of a coating is established; slight adjustments as discussed in paragraph 4.2 may be made if metamerism can be tolerated, but significant modification of absorption in the visible region is unlikely to be allowed owing to established convictions of visible camouflage requirements. Thus, the most effective way to produce a solar heat reflecting coating is to maximize the reflectance of solar energy in the near infrared region of the spectrum.

Solar reflective coatings have been formulated in either of two ways. In the first case, it is possible to produce solar reflective coating systems comprising a highly reflective undercoat and a topcoat which can be coloured with pigments transparent to NIR radiation. The topcoat provides the desired visual colour but does not absorb NIR radiation. The topcoat must be as thin as possible for it will always possess some absorption. Also, for uniform visual appearance the film thickness has to be consistent; this is not always easy when the coating is applied outside a factory. Maintenance is a problem because topcoat and undercoat must be applied at proper thicknesses and intercoat intervals to retain properties, and the cost of a two coat system exceeds that of a single coat.

In so far as visible colour permits, pigments which strongly absorb in the infrared should be avoided in the topcoat of a two coat system. As the near infrared absorptance of the topcoat increases, reflectance from the undercoat is diminished because less energy reaches the undercoat. It is essential to pay particular attention to pigment volume concentration in the topcoat under these conditions.

A preferred solution is to use pigments which are reflective in the NIR to produce a single coating. Blending reflective and transparent pigments gives much flexibility in tailoring infrared properties, and the difficulties of a two-coat system are avoided.

5.3 Thermal Infrared Reflecting (low emissivity) Coatings

These coatings are designed to reduce thermal emission and to reflect incident TIR radiation. Metallic pigments, particularly aluminium flakes, reflect strongly across the TIR region and are the principal active ingredient in these coatings. The best aluminium paints for this purpose are those made with extra brilliant grades of aluminium flake which have larger particle sizes. Pigments which overlap in a systematic manner, known as leafing pigments, have been shown to produce greater reflectance than nonleafing pigments [32], and this has been ascribed to the complete hiding of the resin by the leafing metal flakes in the matrix. Aluminium paints reflect thermal infrared with greater efficiency than they reflect white light. Black coatings are commercially available [34] which offer low solar reflectance and high thermal reflectance (0.9), i.e. thermal emissivities of 0.1. It is understood that these materials have been trialled on NATO tanks, however the high solar collection efficiency of this material would require that its use in tropical and subtropical environments be closely engineered.

Table 5 shows the temperature transfer properties of a steel panel coated on the illuminated side with the standard Australian Navy grey paint compared to one painted on the illuminated side with a leafing aluminium paint.

5.4 Camouflage Coatings

Camouflage coatings adjust the normal reflectance of an object so that it resembles its immediate environment, thus making it nearly indistinguishable from its surroundings under natural as well as artificial illumination. Camouflage coatings must reflect both visible light and infrared radiation to the same degree as their surroundings. For terrestrial applications, the most important environments where concealment is desired are foliage and desert regions.

Table 5: Effect of paint composition on thermal emission

Time (minutes)	Temperature Rise (°C) [a] Sides 1 and 2 Std Australian Navy grey paint[b]	 Side 1 aluminium paint[c] Side 2 Std Australian Navy grey paint
0	31.0	31.0
1.0	63.0	46.0
2.0	84.0	56.0
3.0	98.0	63.0
4.0	106.0	69.0
5.0	112.0	72.5
6.0	115.0	76.0
7.0	117.0	78.0
8.0	119.0	80.0
9.0	121.0	81.5
10.0	123.0	81.5
15.0	125.5	81.4

[a] Panels at room temperature (20°C) at time = 0.
[b] Both sides painted with grey paint.
[c] Irradiated side painted with aluminium paint, reverse side painted with grey paint.

Pattern painting with various camouflage colours can also break up the silhouette of an object and make it less conspicuous. For maximum effectiveness, the various coatings used in the pattern must be significantly different in both optical and infrared reflectance [35]. Coatings having low emissivity are used to minimize temperature contrasts between vehicles exposed to solar radiation and their surroundings. They are most effective when the emissivity varies between patches of paint and the infrared outline of the vehicle is masked.

5.4.1 Coatings for Forest and Jungle Areas

Pigments used to produce green coatings for these areas are selected for their ability to duplicate the reflectance properties of chlorophyll, the green pigment responsible for the characteristic colour and high infrared reflectance of vegetation. The reflectance spectrum of chlorophyll shows a peak near 550 nm, low values in the visible red region, a dip in the far visible red at 650-680 nm, a sharp rise between 680 and 710 nm, and uniformly high values above 720 nm. The goal for woodland camouflage coatings is to match this spectrum. Coatings for camouflage must control reflectance in the NIR between 700 and 1200 nm; the band between 700 and 900 nm is most important [36].

Most specifications for camouflage coatings require a sharp rise in reflectance between 700 and 720 nm, and require that the average reflectance in the 700 to 900 nm region exceeds the average reflectance in the 600 to 690 nm region. Such coatings approximate the reflectance spectrum of chlorophyll and appear in the NIR to have the same reflectance as natural vegetation.

Many green pigments resemble the colour of chlorophyll but, unlike chlorophyll, show strong absorption in the NIR. Chromium trioxide is green in colour and possesses a reflectance curve similar to that of chlorophyll, and was the principal pigment in early NIR camouflage paints. For some specifications which do not call for reflectance to rise rapidly in the NIR, chromium trioxide tinted to the desired visual shade can still be used as the basic pigment. When infrared photography or modern detection methods are used, however, these pigments are readily detected as dark shadows against a light background of natural vegetation.

Older formulations based on lead chromate (chrome yellow), basic lead chromate (chrome orange) and molybdated lead chromate (moly orange), and tinted with blue and red pigments, produce camouflage coatings in a variety of green shades [37], but their use has been curtailed in the United States because of their extremely high lead content.

A range of visual colours is used for modern camouflage coatings. Each colour is specified by its brightness Y and its chromaticity coordinates x and y. These parameters are defined by the International Commission on Illumination, known as CIE from its name in French, Commission Internationale d'Eclairage. The desired colour is plotted as a point on a chromaticity diagram, and colour tolerance is stipulated by a boundary on which lie all points which differ from the target colour by the same visual difference. The boundary normally takes the form of an ellipse, as shown in Figure 3 for US forest green camouflage paint [38]. In this case the visual difference is stipulated by the obsolescent NBS [for (US) National Bureau of Standards] unit, which is computed using complex equations from the Y, x and y values of the standard and sample colours [39].

Infrared reflectance is specified in various ways. British Material Specification DTD 5618 [40] stipulates minimum values of reflectance at 700, 800, 900, 1000, 1400 and 2000 nm for each of eleven colours. In the United States, the infrared reflectance is specified by a narrow range of permissible values as shown in Figure 4. Chromium oxide alone cannot meet this requirement. Cobalt chromite spinels containing small amounts of zinc and titanium are the most effective pigments for this purpose and are tinted to the desired spectral properties with iron and chromium oxides and organic yellows, browns and violets. The optical brightness (Y), the average reflectivity in the 600 to 900 nm band, and the reflectivity ratio of the band at 700 to 900 nm to the band at 600 to 690 nm are also specified for forest green camouflage paint [39].

A solar heat reflecting lusterless olive drab enamel conforming to Australian Specification 7650/ADF(M) 146-1 [41] has been produced in the present study from some of the pigments in Table 4. This coating has a reflectivity of 42% at 800 nm and a gloss of 1. The formulation of this coating is given in Table 6.

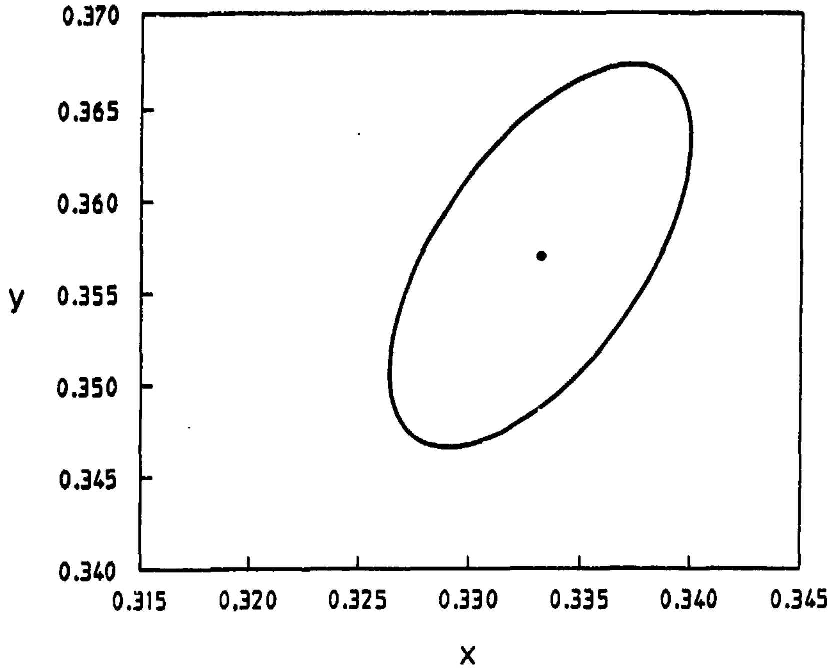

Figure 3: *Chromaticity diagram for Forest Green camouflage paint.*

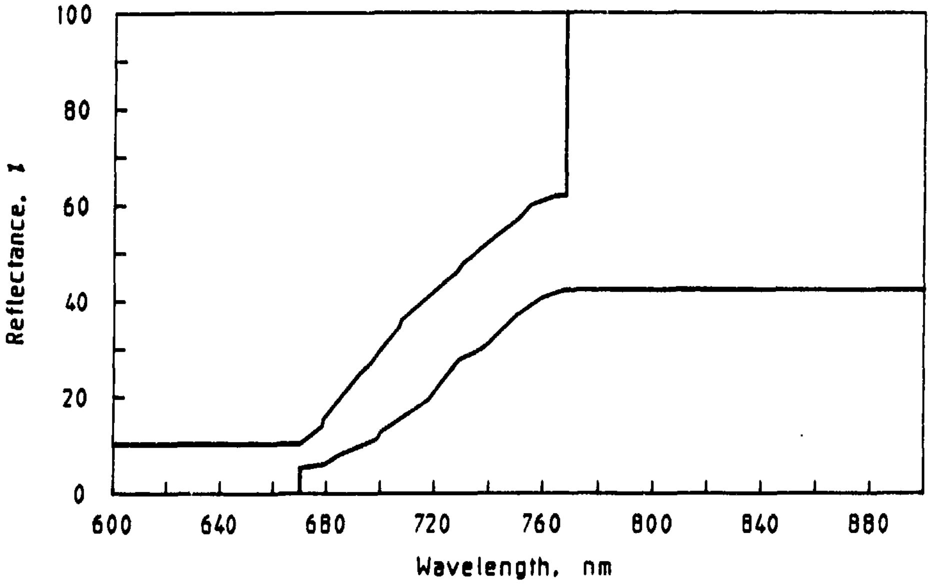

Figure 4: *Permissible infrared reflectance values of US Forest Green.*

Table 6: Solar heat reflecting olive drab camouflage enamel

Ingredient	Oil Absorption	Specific Gravity	Kilograms	Litres
Chromium Oxide[a]	22	5.12	64.20	12.58
Red Iron Oxide[b]	18	4.90	3.72	0.76
Yellow Iron Oxide[c]	36	4.03	10.55	2.65
Titanium Dioxide, 10 µm[d]	17	3.90	51.86	13.32
Magnesium Silicate[e]	45	2.75	37.14	13.51
Silicone Alkyd Resin, 70%[f]		0.96	85.37	85.31
Cobalt Octoate, 6%[g]			0.60	0.67
Calcium Octoate, 20%[h]			2.44	2.65
Zirconium Octoate, 20%[i]			0.50	0.45
Methyl Ethyl Ketoxime[j]			4.00	3.80
White Spirit[k]		0.79	20.93	25.25
TOTAL			281.31	160.95

[a] Chrome oxide G8599, Commercial Minerals Ltd.
[b] Red iron oxide RO-4097, Commercial Minerals Ltd.
[c] Yellow iron oxide YO-2087, Commercial Minerals Ltd.
[d] Tiona VC, SCM Chemicals Ltd
[e] Talc TSF, Commercial Minerals Ltd.
[f] Kemsil 2425/70, Kemrez Chemicals Division, ICI Aust. Ltd.
[g] Hardadri cobalt, Colours & Chemicals Pty Ltd.
[h] Hardadri calcium, Colours & Chemicals Pty Ltd.
[i] Hardadri zirconium, Colours & Chemicals Pty Ltd.
[j] Exkin number 2, A.C. Hatrick Chemicals Pty Ltd.
[k] White spirit, Shell Chemicals (Australia) Pty Ltd.

5.4.2 *Coatings for Desert Regions*

For these regions, natural sand and earth colours in a range of grey, orange, red, yellow and earth colours must be reproduced. For desert colours and woodland browns and black, iron oxides ranging from red to yellow to black are used. Carbon black absorbs strongly throughout the infrared and is usually proscribed in camouflage coatings, although trace levels (0.01%) can sometimes be used to bring the infrared reflectance down into specified levels. In recent times, formulations have been prepared to increase NIR reflectances to match higher reflectances in specific desert regions.

5.4.3 *Coatings for Ocean Environments*

Paints now used on the hulls and superstructures of warships often exhibit relatively high solar absorption because of the grey colours required for visual camouflage. These colours may vary from bluish to greenish grey depending on the waters in which the vessel is likely to operate, and have reflectances near 30%. High solar absorption necessarily results in high surface temperatures which reduce the comfort of the crew, increase cooling requirements and, more significantly, amplify the emission of thermal radiation. Other methods of cooling hot exposed surfaces, such as using water spray, reduce thermal emissions but add power requirements and topweight to the ship.

Most of the common blue and black pigments absorb infrared radiation strongly, and even small amounts are effective in reducing infrared reflectance. Historically, naval coatings have contained significant amounts of carbon black [42, 43]. An early attempt [44] to formulate without carbon black produced solar heat reflecting coatings and low emittance coatings containing 15% of powdered aluminium [45, 46]. These coatings had poor weatherability and colour retention because antimony sulfide, a black pigment used in place of carbon black, is unstable and reacts with air to form white antimony oxide on prolonged exposure.

Effective solar heat reflective coatings have now been made in the grey shades established for warships. Carbon black has been replaced by an organic perylene black which absorbs strongly in the visible region but is transparent throughout the infrared. The formulation for a full gloss Australian naval coating conforming to Light Grey 631 [47] developed in the present study is given in Table 7. This coating reflects 77% of solar radiation at 800 nm in comparison to the standard coating which reflects 33% and has a 60° gloss of 74. Table 8 contains a formulation also developed in the present study for a semigloss solar heat reflecting coating for U.S. naval warships which has a haze grey colour [48] and a 60° gloss of 50. The spectral reflectance from 380 to 2300 nm is shown in Figure 5 for this coating and for the conventional coating. The reflectance of the new coating is approximately twice that of the older coating in the region from 720 to 2300 nm. The reflectance in the visible region between 380 and 720 nm indicates that the new colour is metameric to the older colour; this is a consequence of substituting phthalocyanine blue and red iron oxide for carbon black.

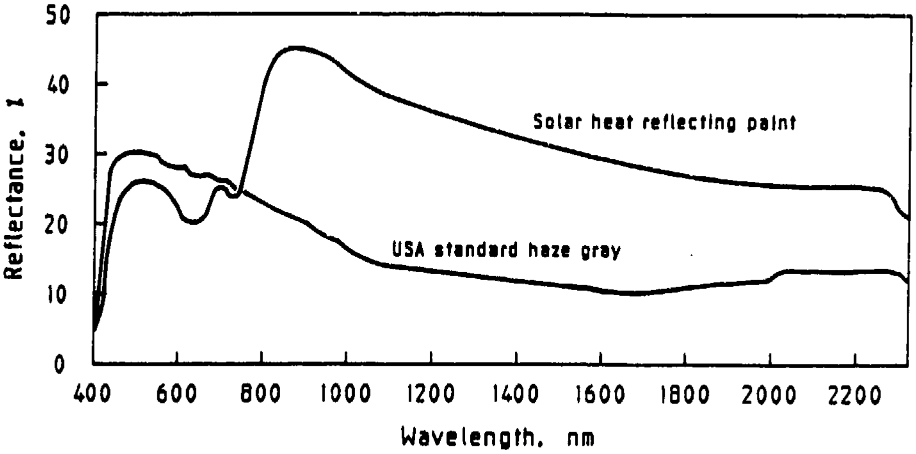

Figure 5: Infrared reflectances of two Haze Grey formulations.

Table 7: Solar heat reflecting Light Grey camouflage enamel

Ingredient	Oil Absorption	Specific Gravity	Kilograms	Litres
Titanium dioxide, 200 nm[a]	17	4.00	9.20	2.30
Titanium dioxide, 10 µm[b]	17	3.90	84.15	21.65
Magnesium silicate[c]	45	2.75	10.34	3.74
Yellow iron oxide[d]	36	4.03	0.31	0.07
Paliogen black[e]	37	1.43	1.76	1.24
Silicone alkyd resin, 70%[f]		0.96	112.53	113.66
Cobalt octoate, 6%[g]			0.73	0.83
Calcium octoate, 20%[h]			2.95	3.21
Zirconium octoate, 20%[i]			0.60	0.53
Methyl ethyl ketoxime[j]			3.35	3.33
White spirit[k]		0.79	13.06	15.78
TOTAL			237.98	166.34

[a] Ti-Pure R-960, duPont Australia Ltd.
[b] Tiona VC, SCM Chemicals Ltd.
[c] Talc TSF, Commercial Minerals Ltd.
[d] Yellow iron oxide YO-2087, Commercial Minerals Ltd.
[e] Paliogen black L0084, BASF Australia Ltd.
[f] Kemsil 2425/70, Kemrez Chemicals Division, ICI Australia Ltd.
[g] Hardadri cobalt, Colours & Chemicals Pty Ltd.
[h] Hardadri calcium, Colours & Chemicals Pty Ltd.
[i] Hardadri zirconium, Colours & Chemicals Pty Ltd.
[j] Exkin number 2, A.C. Hatrick Chemicals Pty Ltd.
[k] White spirit, Shell Chemicals (Australia) Pty Ltd.

5.4.4 *Coatings for aircraft*

Strict countershading principles are used by the U.S. Navy on maritime reconnaissance aircraft which involve the darkest colour on top, intermediate on the sides and lightest shade underneath. This system is used as detection from above will involve the aircraft against a sea background which has a reflectance factor to sunlight of less than 3% [49]. Viewed against a clear sky, the relative effect of paint schemes is related to the direction of view to the sun. White aircraft appear lighter than the sky when viewed down sun so light grey colours are employed. The thermal load from insolation into the P3-C aircraft painted with the U.S. Navy grey paint (which is a low infrared reflecting paint) has been determined to be 1.7 kW more than that for the same aircraft with white top half fuselage and all other surfaces grey which is the RAAF 1990 colour scheme [50]. The air temperature for this comparison was 33°C. The infrared reflectances of the high NIR reflecting paints were compared to those of standard paints of the same visual colours and are shown in Table 9. In theory, these grey colours should reduce the heat load by 50% compared to painting in standard grey colours.

Table 8: Solar heat reflecting Haze Gray camouflage enamel

Ingredient	Oil Absorption	Specific Gravity	Kilograms	Litres
Titanium dioxide, 200 nm[a]	17	4.00	327.80	6.96
Titanium dioxide, 10 µm[b]	17	3.90	82.37	21.15
Magnesium silicate[c]	45	2.75	10.33	3.74
Yellow iron oxide[d]	36	4.03	2.19	0.53
Red iron oxide[e]	18	4.90	2.40	0.49
Phthalocyanine blue[f]	45	1.65	0.70	0.41
Silicone alkyd resin, 70%[g]		0.96	115.44	120.43
Cobalt octoate, 6%[h]			0.79	0.90
Calcium octoate, 20%[i]			3.22	3.52
Zirconium octoate, 20%[j]			0.66	0.56
Methyl ethyl ketoxime[k]			5.08	5.03
White spirit[l]		0.79	25.80	31.15
TOTAL			275.78	194.87

[a] Ti-Pure R-960, duPont Australia Ltd.
[b] Tiona VC, SCM Chemicals Ltd.
[c] Talc TSF, Commercial Minerals Ltd.
[d] Yellow iron oxide YO-2087, Commercial Minerals Ltd.
[e] Paliogen black L0084, BASF Australia Ltd
[f] Sunfast blue 15:2 248-0532, T.R. Chemicals (Aust) Pty Ltd.
[g] Kemsil 2425/70, Kemrez Chemicals Division, ICI Australia Ltd.
[h] Hardadri cobalt, Colours & Chemicals Pty Ltd.
[i] Hardadri calcium, Colours & Chemicals Pty Ltd.
[j] Hardadri zirconium, Colours & Chemicals Pty Ltd.
[k] Exkin number 2, A.C. Hatrick Chemicals Pty Ltd.
[l] White spirit, Shell Chemicals (Australia) Pty Ltd.

Table 9: NIR reflectances of standard paints and solar reflecting paints for Orion camouflage paint scheme

Y	Standard Paint	NIR Reflecting Paint
49.5	52%	77%
37.5	43%	70%
23.5	24%	61%

6. Summary

Relevant physical laws governing the response of coatings to solar and infrared radiation have been reviewed. The reflection of infrared radiation by a paint is controlled primarily by the refractive index and particle size of the pigments in the coating. Pigments have been evaluated for reflectance, transparence and hiding power in the near infrared region, and guidelines for pigment slection for various applications given in terms of their optical properties in the near infrared region. Raw materials selection, manufacture and evaluation of coatings have been discussed with respect to tailoring infrared reflectance. By employing the principles developed herein and using pigments with appropriate properties, organic coatings have been developed which are consistent with the visible colour requirements of the Australian and US Navies. Significant increases in the reflection of infrared radiation have been demonstrated by the new formulations. The need for a very clear understanding of the threat systems and the operational conditions of service platforms has been emphasised. It is only with this understanding that optimum paint schemes can be devised. However, it can be stated that the use of the solar infrared reflecting paints described herein would reduce conspicuity of isolated platforms to surveillance and seeker systems operating in the mid and far infrared without detriment to visual camouflage characteristics.

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