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Pigmentation of a Camouflage Dye and Investigation of Its Colour and Reflectance Properties

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Natural foliage and terrain reflect light both in the visible (380-700 nm) and near infrared (700-900 nm) regions of the electromagnetic spectrum. In this study, dyes consisting of several different pigment combinations are proposed intended to meet the camouflage needs fitting the reflectance properties of local natural green foliage in both visible and near infrared regions. Camouflage pigment green 179, functionalized with the appropriate infrared reflectance was mixed with varying amounts of chromium oxide, iron oxide and carbozel violet pigments and the spectral reflectance of surfaces treated with this alkide based dye was measured in the 320-1500 nm interval. Chromaticity and observed brightness (Y) values were determined using the CIELAB 1976 (L* a* b*) colour definition systems. Field tests demonstrate that dyes thus obtained, meet camouflage standards in both the visible and near infrared regions.

Key Words: Infrared reflectance, Camouflage, Dye, Pigments.

INTRODUCTION

Reflectance is one of the three behaviours of light when interacting with matter interaction. Different objects have different tendencies to selectively absorb, reflect or transmit light of certain frequencies. When light waves interact with an object that exhibits a refractive index differing from the medium of light wave propagation, a portion of the light is reflected from the object. Per cent reflectance expresses the amount of light energy reflected from an object at a specific wavelength. Reflectance can be specular (glossy) or diffuse (surface scattered). Specular reflectance consists of light reflecting at an angle opposite that of the incident angle. Mirrors (and glossy surfaces) exhibit large degrees of specular reflectance. Diffuse reflectance occurs when incident light is reflected at a multitude of angles from a surface. Reflectance is the reason why objects appear with a various different colours[1].

Every day language descriptions of colours can be expressed in an infinite number of ways. In addition to this, the appearance of a colour can change in different circumstances, such as the colours and lighting conditions of the surroundings. These difficulties are of great practical importance when trying to describe a colour that needs to be reproduced in a recipe by colour technologists in a dyeing process. To overcome this, a standard system has been developed and refined over the years by the CIE. The aim of which is to say how a particular colour might be reproduced by mixing the three red, green and blue primary light sources rather than trying to describe it in words[2].

Objects that reflect colours close to the environments they are considered 'camouflaged'. Camouflage means to deceive or disguise and conceal reducing the possibility of detection. In military terminology it is used for a system that disguises personnel and equipment against detection by the enemy. As military forces became more advanced and sophisticated in their striking power, equipment and weaponry, importance of camouflage for the protection of lives and equipment became more important[3]. In present days, to function against remote sensing equipment and detection applications, camouflage is applied not only in the visible region but in a much wider area of the electromagnetic spectrum. Remote sensing is the process of acquiring information from the environment by the use of sensors that is not in physical contact with the object under study. Remote sensing and detection are predominantly military applications and have been widely discussed for the infra-red region[4].

Wang *et al.*[5] have reported, in detail, on a multitude of organic materials and polymers functionalized as to absorb in the near infrared region (1000-2000 nm) utilized in photonics and telecommunications. The general methodology of molecular design and characterization of infrared absorbing dyes and their utilization in high technology applications such as laser optical recording systems, laser printing systems, laser thermal writing displays, medical or biological applications and infrared photography have been reported in detail[6].

Unfortunately, information on pigments, pigment mixtures reflecting in the near infrared region (700-1500 nm) cannot usually be found in literature and most of the data is usually restricted to patented applications. An excellent study on such pigments, together with reflection mechanisms in the near infrared, advantages of infrared reflecting coating, factors influencing infrared reflection and some patented preparation procedures were given by Bendiganavale and Malshe[7].

Infrared reflective pigmentation science utilizes the unique properties of specialty pigments to achieve a colour of choice by reflecting (or absorbing) the correct wavelengths of energy and controlling to emissivity to benefit of the user. Infrared reflective pigmentation technology allows the user to achieve a specific colour space in the visible light range, while reflecting light in the near infrared range of the electromagnetic spectrum.

Dyes and coating that can simultaneously mimic both the visible and infrared reflection values of natural foliage can be used to conceal critical and important military assets from the naked eye and infrared night vision equipment of the enemy. In the infrared region, this is achieved by coating and painting such assets in such a way that their reflection properties in the 700-1500 nm region match the reflectance trend of the background.

In the present study, formulations for forest green infrared reflecting dyes based on the MIL-C-46168[8,9] standard were prepared dye formulations containing 20-25 % pigments by weight and each mixture was within the standard reflection values and CIELAB chromaticity coordinate system intervals. Chromaticity coordinates and reflectance values of surfaces coated with these dyes were measured in the 320-1500 nm region according to the spectral reflectance principle. The CIE 1931 standard colorimetric system was used and the results are reported for the 2º standard observer.

EXPERIMENTAL

In this study, the pigments in the composition of the IR reflecting dye is reported in accordance with the MIL-C-46168-(ME) standard[8]. The pigments, filler material, other constituents and their origins are reported in Table-1.

TABLE-1
PIGMENTS AND ADDITIONAL MATERIALS USED IN FORMULATION

Materials	Colour Index	Manufacturer	Trade Mark
Pigment green* (PG)	Pigment green	Shepherd	Camouflage green 179
Chrome oxide green (COG)	Pigment green 26	Indigenous Source	Chrome oxide green 26
Chrome orange (CO)	Pigment yellow 34	Indigenous Source	Chrome orange 34
Chrome oxide yellow (COY)		Indigenous Source	Chrome oxide yellow
Ferric oxide red (FOR)		Indigenous Source	Red ferric oxide
Ferric oxide (FOB)	Pigment black 30	Shepherd	Black 10C909
Carbon black (CB)		Degussa	Printex-U
Carbazole Violet (CV)	Pigment violet 23	Clariant	Carbazole Violet
Talk		Omya	OMYATALC 20-KP
Barite		Omya	Barite
Calcite		Omya	OMYACARB 40-KP
Matting agent		Degussa	Acematt TS 100
UV Absorber		Bayer	(1,2,2,6-pentamethyl-4-piperidyle)
Precipitation prevention		Bayer	Product U
Resin		Bayer	Desmophen 650 MPA
Solvent		Merck	Methyl Ethyl Ketone
Hardener		Bayer	Desmodur N75 MPA

*Non acid dissolving green pigment.

A Perkin-Elmer Model Lambda 900 UV/VIS/NIR spectrometer equipped with a PELA-1000 150 mm integrating sphere accessory and utilizing the UV-WinLAB colour software was used in reflectance measurements. The equipment was calibrated with high purity $BaSO_4$ disk (Spectralon®). Experimental plates were tested using a center mounted sample holder at angles between 0 and 180º.

Preparation of the dye: Standards specify pigments, reflectance limits, colour, observed brightness and chromaticity coordinates, but not the pigment ratios. In the present study, the dyes were prepared by mixing 20-25 % resin, 20-25 % pigment, 15-20 % filler, 5-7 % other additives and solvent. A laboratory type Sheen DISPER master with a special design stirring blade was used to disperse the green pigment in organic resin for 10 min at 300-900 rpm. The rest of the constituents were then added and mixing was resumed for 10 more minutes at 2000 rpm. Viscosity was adjusted to 900 cP (*ca.* 85 KU) by the addition of solvent and was monitored with a Brook Field type viscometer. The dye was then applied to cardboard plates with a doctor blade and was left to dry for 2 days.

Different samples were prepared by varying the amounts of the pigments and the resulting IR reflectivity values, chromaticity coordinates and placement in the colour space were determined for each sample. The (x, y) chromaticity coordinates and L*a*, b* values were compared to the standard. Resin, fillers and other additives do not affect the IR reflectivity, colour space placement and chromaticity coordinates. Therefore, the amounts for these components were held constant across the samples. In order to study the effects on the reflectance values amounts of the seven pigments, namely, green, chrome oxide green, chrome oxide yellow, iron oxide red, iron oxide black and carbazole violet were changed. Reflection values were measured and amounts were systematically adjusted to obtain the chromaticity intervals of the standard. The experimental protocol reported in Table-2 was used in preparing the pigment mixtures.

TABLE-2
EXPERIMENTAL PROTOCOL FOR PREPARING PIGMENT MIXTURES

Run #	Pigments							
	PG	CB	FOB	COG	FOR	COY	CV	CO
1	**16**	**0.6**	0.0	9	0.6	0.6	0.6	7
2	**22**	**0.6**	0.0	9	0.6	0.6	0.6	7
3	**16**	0.0	**0.6**	9	0.6	0.6	0.6	7
4	**22**	0.0	**0.6**	9	0.6	0.6	0.6	7
5	16	0.0	0.6	**0**	**0.0**	0.6	0.6	7
6	16	0.0	0.6	**0**	**0.6**	0.6	0.6	7
7	16	0.0	0.6	**0**	**1.2**	0.6	0.6	7
8	16	0.0	0.6	**9**	**0.0**	0.6	0.6	7
9	16	0.0	0.6	**9**	**1.2**	0.6	0.6	7
10	16	0.0	0.6	**15**	**0.0**	0.6	0.6	7
11	16	0.0	0.6	**15**	**0.6**	0.6	0.6	7
12	16	0.0	0.6	**15**	**1.2**	0.6	0.6	7
13	16	0.0	0.6	**15**	**0.6**	0.0	0.0	7
14	16	0.0	0.6	9	0.6	**0.0**	**0.3**	7
15	16	0.0	0.6	9	0.6	**0.0**	**0.9**	7
16	16	0.0	0.6	9	0.6	**0.3**	**0.0**	7
17	16	0.0	0.6	9	0.6	**0.9**	**0.0**	7
18	16	0.0	0.6	9	0.6	**0.9**	**0.9**	7

RESULTS AND DISCUSSION

Reflectance: Reflectance values of the experimentally prepared plates were recorded in the 320-1500 nm region with a Lambda 900 model UV/VIS/NIR spectrophotometer and selected runs are reported in Fig. 1. With the exception of the first two trials, all reflectance values meet the requirements and tolerances of the standards[8,9] in the 690-900 nm range for light green, forest green, dark green and olive green.

When total infrared reflection values are compared, the dyes of Run #1 and Run #2 are outside the standard limits. When iron oxide black is substituted for carbon black (Run #3) the dye stays within standard limits. The required values are as follows: colour, (Green 383 (34094) according to the FED-STD-595; central chromaticity coordinates (x=0.333 and y=0.357); observed luminance (Y) 5.8-7.5 and L* a* b* 34±1, -6.5±0.5 and 10±0.5 respectively[8]. Since the reflectance value of conventional carbon black is below 40 %, it adversely affects the reflectance value of the dye[3].

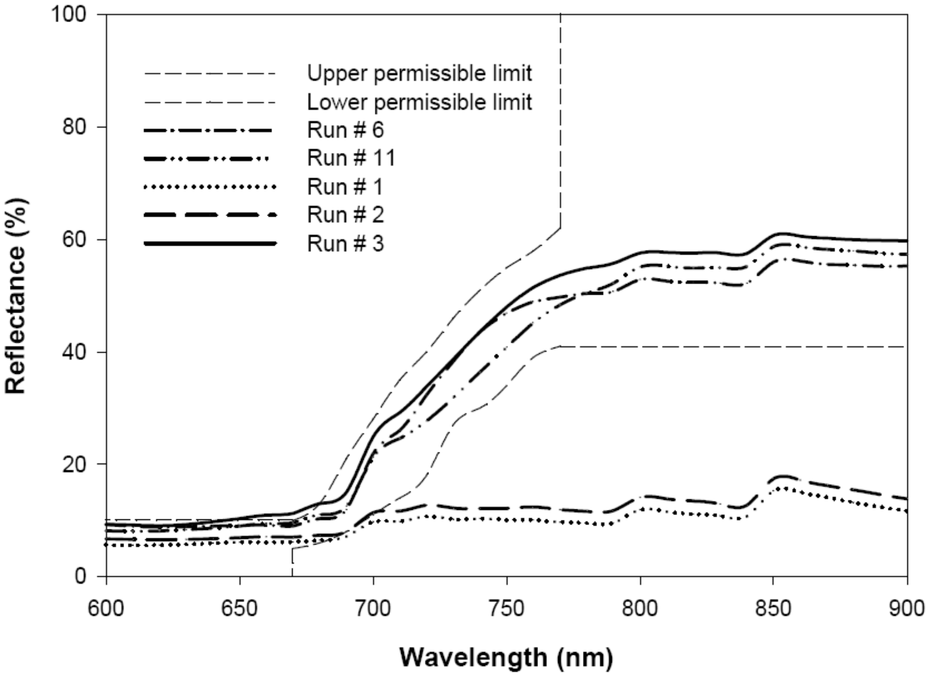


Fig. 1. Total reflectance spectra of selected samples

When mixed with the other pigments, carbon black absorbs more than it reflects and masks the IRR camouflage value of the dye. In regions of green foliage, military camouflage applications use conventional green pigments. Chlorophyll is responsible for the green colour of the foliage and is known that in the 700-900 nm region, which is important for camouflage, conventional green pigments absorb infra-red light while chlorophyll reflects it[7]. For his reason, dye mixtures which fail to meet the standards appear as dark patches within a bright environment.

Coordinates in colour space: The pigment combinations used in the study, generally do not reflect in the 380-700 nm region of the electromagnetic spectrum, although some low amplitude peaks are present[3]. The reflectance spectra of each dye were input to the UV-Winlab software to calculate the chromaticity coordinates, observed luminance and L* a* b* values for the plates. Thus, the colour space positions of the green dyes' on these surfaces were determined. These values for dyes obtained with varying pigment combinations (see grey shaded areas in Table-2) are reported in Table-3.

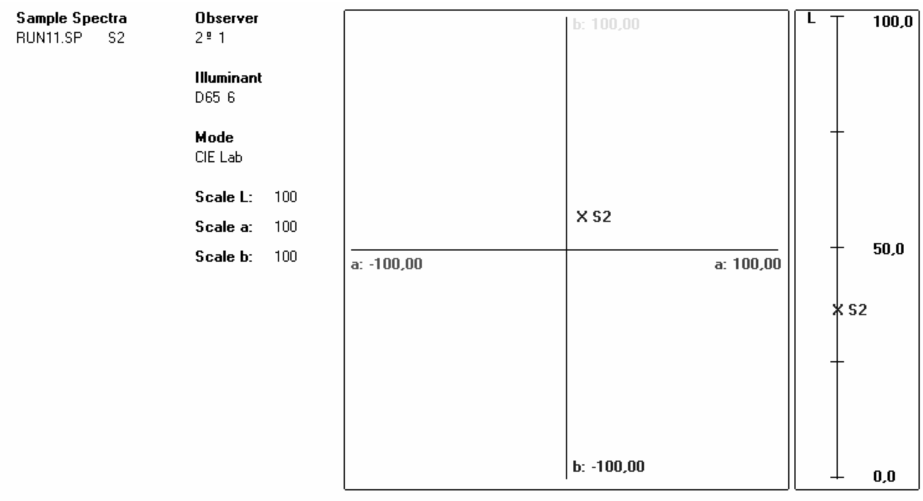
TABLE-3
CHROMATICITY COORDINATES, OBSERVED LUMINANCE AND L* a* b* VALUES

Run #	Chromaticity		Brightness (Y)	L*	a*	b*
	x	y				
1	0.3272	0.3584	5.80	28.90	-2.58	5.38
2	0.3269	0.3613	6.90	31.57	-3.33	6.11
3	0.3544	0.3811	8.64	35.29	-1.59	12.33
4	0.3533	0.3794	8.46	34.92	-1.48	11.86
5	0.3367	0.3745	8.67	35.33	-4.06	9.61
6	0.3468	0.3733	8.54	35.08	-1.67	10.30
7	0.3497	0.3676	8.43	34.87	0.08	9.60
8	0.3327	0.3867	8.60	35.21	-7.21	11.18
9	0.3443	0.3774	8.35	34.70	-2.96	10.64
10	0.3260	0.3790	8.72	35.44	-7.25	9.40
11	0.3370	0.3883	8.86	35.72	-6.65	11.93
12	0.3376	0.3777	8.48	34.96	-4.46	10.13
13	0.3364	0.3883	9.75	37.38	-7.01	12.26
14	0.3472	0.3869	8.77	35.53	-4.22	12.63
15	0.3432	0.3719	7.75	33.45	-2.09	9.44
16	0.3483	0.3972	9.60	37.12	-6.07	14.83
17	0.3507	0.4000	10.11	38.03	-6.18	15.81
18	0.3359	0.3710	8.58	35.17	-3.53	8.94

The results of the first four runs indicate that camouflage green pigment does not have an appreciable effect on the CIE 1931 chromaticity coordinates and the position in the CIE 1976 L* a* b* space. Based on this outcome, the amount of the green pigment was minimized for the last run.

Results of Run #1 and Run #2 indicate that the main effect of the carbon black pigment is on visible brightness and L* has no reflection in the near infrared region. (Run #1 and Run #2 in Fig. 1). On the other hand, carbon black reduces visible brightness below standard's limits and darkens L*. Limits of the standard are met when iron oxide black is substituted for carbon black as was done in Run #3 and Run #4.

Fig. 2 shows the coordinates of the Run #11 green dye in CIELAB 1931 system with 2º observation angle. The negative 'a' value indicates that the dye is green and the positive 'b' shows a shift to yellow. The a, b values in Fig. 3 when taken together indicate that all the prepared dyes are green and the negative 'a' values indicate yellowish green. Fig. 3. reports a and b values with the specification limits.



Sample Spectra
RUN11.SP S2

Observer
2º 1

Illuminant
D65 6

Mode
CIE Lab

Scale L: 100
Scale a: 100
Scale b: 100

Fig. 2. CIELAB system L* a* b* values

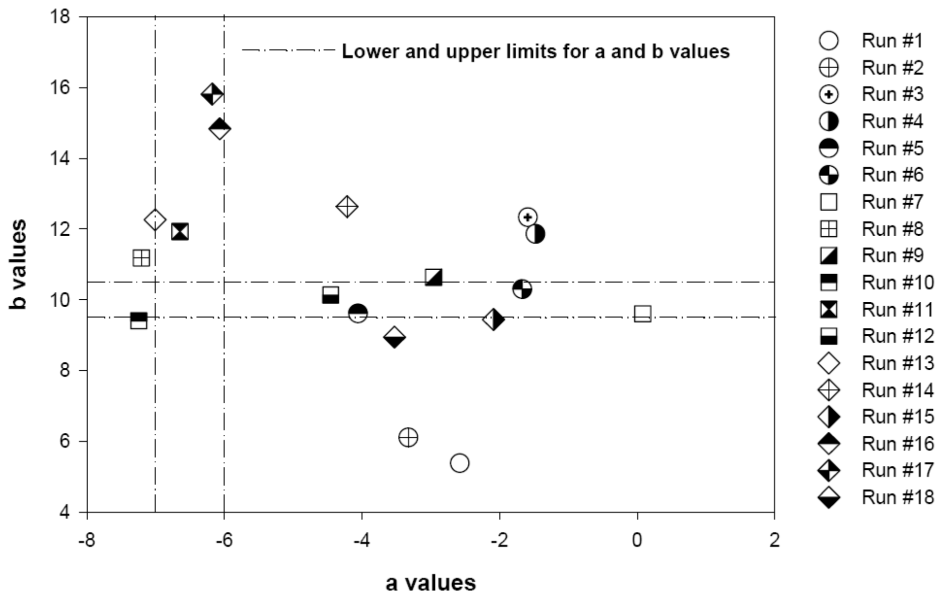


Fig. 3. Colour coordinates of the samples

Fig. 4 illustrates large chromaticity coordinate deviations of the prepared sample from US Forest Green ellipse. This result shows that the specific location of a dye in the chromaticity coordinate system is in fact closely related to the pigment ratios of the dye. For present combinations, the resulting positions are within an ellipse located bounded by 0.325-0.355 for x and by 0.36-0.4 for y. In the present work, pigment ratios were determined according to the experimental protocol reported in Table-2 while the ratios of the oxide mixtures are reported as percentages of the total amount of pigment (Table-4).

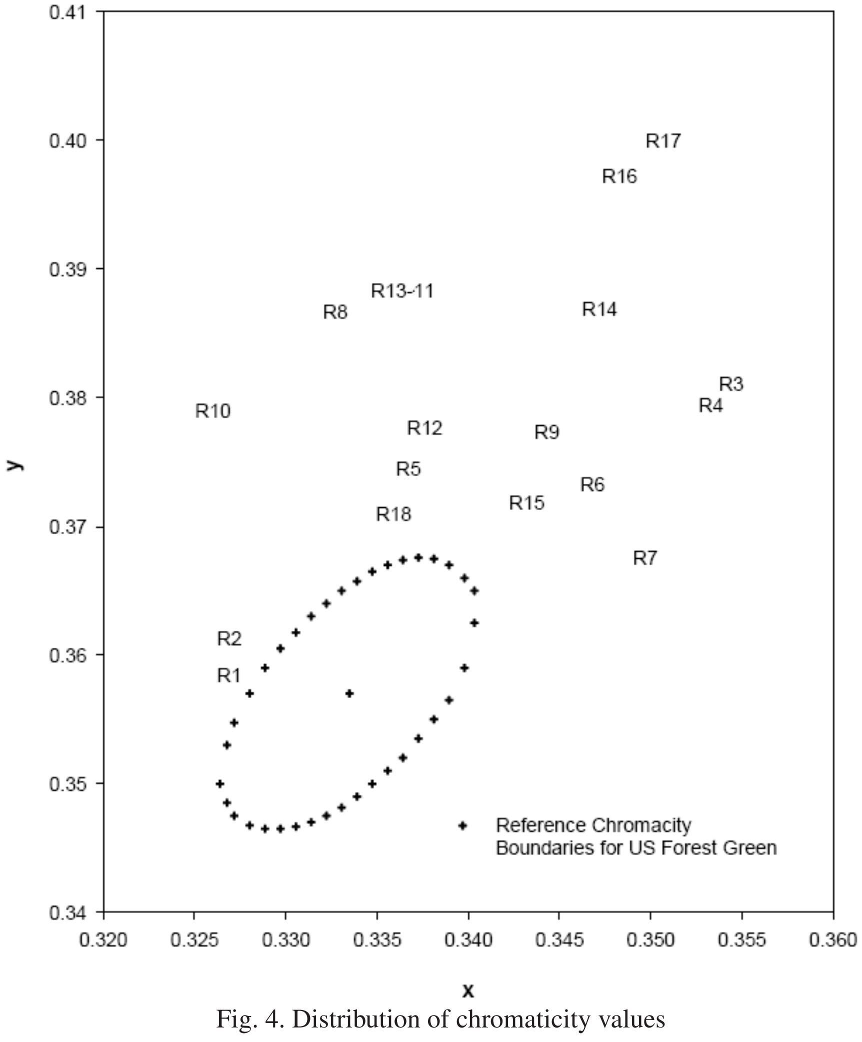


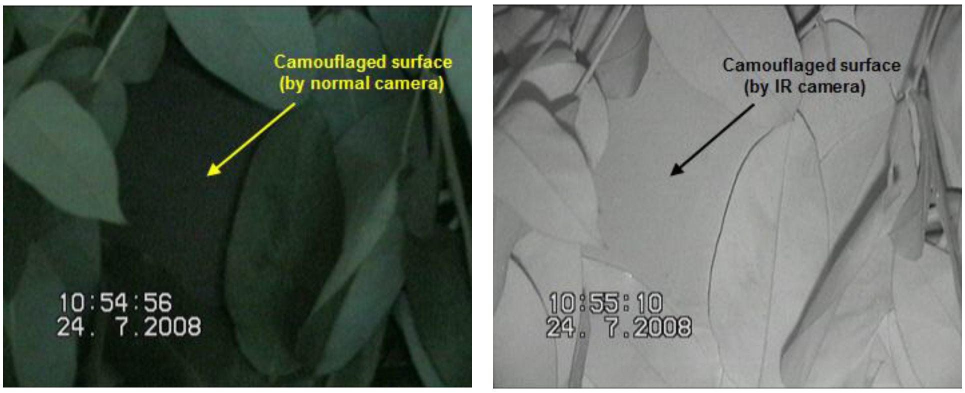
Fig. 4. Distribution of chromaticity values

These ratios were determined simply by requiring that the chromaticity coordinates (x, y) and the (L, a, b) values of the resulting green colour stay within the desired limits.

TABLE-4
LOWER AND UPPER LIMITS OF PIGMENT VALUES

Pigments	Lower-Upper values (g)	Per cent by weight (%)
Camouflage green	16-22	8.95-11.75
Chrome oxide green	10.5-12.0	5.87-6.41
Chrome oxide yellow	0.45-0.9	0.25-0.48
Ferric oxide red	0.45-0.6	0.25-0.32
Carbazole violet	0.60-0.9	0.34-0.48
Chrome orange	9.0	5.03
Ferric oxide black	0.6	0.34

Field testing: The plates prepared to standards for light green, forest green, dark green and olive green were photographed with a Panasonic NV-DS25 digital camera in natural environments. Fig. 5a is daylight photograph of the plate of Run #11 and 5b is the same plate photographed in the infrared mode of the camera. The photographed plate was exposed to the natural environment for 24 months. Results demonstrate that the camouflage plates of the present study yield the same reflectance values as the natural environment both in the visible (380-700 nm range) and IR (600-900 nm range) regions.



(a) (b)

Fig. 5. Appearance of camouflaged surface (a) with normal camera (b) with IR camera

Dye formulations for the light green, forest green, dark green and olive green were successfully prepared within the reflectance limits of the standard. Upper and lower limits of the required ratios are reported as weight per cent. Carbon black reduces reflectance in the NIR region. This handicap may be overcome by substituting iron oxide black for carbon black. The prepared surfaces yield the same reflection trend as the natural environment both in the visible and the 600-900 nm (the working range of night vision equipment) regions providing an effective camouflage. Angles of reflection did not have an observable effect on this conclusion. This may be explained by the fact that the surfaces' reflections are diffuse rather than specular.

Constituents other than the pigments may be used in constant quantities since they do not affect the values required by the standard specifications. The limiting values of the pigment percentages might be used to design response surface or simple factorial design experiments in future work. The dyes might thus be easily formulated to abide the required specifications.

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