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FEASIBILITY OF USING FLUORESCENT COLORANTS TO
AFFORD CAMOUFLAGE PROTECTION
AGAINST PHOTOGRAPHIC DETECTION

by

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FOREWORD

This report considers the problem of resolving two camouflage requirements that appear to be incompatible. When faced with situations of this type, decision-makers are tempted to make compromises that do not entirely satisfy either requirement. The approach pursued in this study is novel in that it attempts to avoid compromise by taking advantage of unique colorant properties under different environmental conditions. It is hoped that the study will lead to a solution that satisfies both requirements.

The work reported is being continued in several parallel directions, including an extension of the survey of dyes, studies of chemical factors involved, and development of dye formulations for various fabrics.

For their comments on this work and help in obtaining many of the dyes that are reported, the writers wish to thank the following members of the NAS-NRC Committee on Textile Dyeing and Finishing:

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ABSTRACT

Camouflage against visual observation or detection by infrared image-converters requires that the reflectance of objects be relatively low. On the other hand, camouflage against infrared-sensitive photography requires that reflectance in the appropriate spectral region be relatively high. Reasons for these restrictions are discussed.

Of possible approaches to attain desired reflectance characteristics, that involving fluorescence in the near infrared is discussed. A methodology for searching for suitable dyes and the design of an instrument that can identify the invisible infrared fluorescence are described. The infrared fluorescence characteristics of over 100 dyes applied to various fabrics is given.

FEASIBILITY OF USING FLUORESCENT COLORANTS TO AFFORD CAMOUFLAGE PROTECTION AGAINST PHOTOGRAPHIC DETECTION

1. Introduction

Modern technology can now provide a military observer with means to detect objects of interest with a variety of detection systems. Some of these systems have been designed for use under special conditions, but collectively they are sensitive in parts of a wide region of the electromagnetic spectrum from the ultraviolet to the microwaves. (1-14)

When designing camouflage systems, it is necessary that solutions for the various spectral regions and various detection systems be compatible with each other. A single uniform should afford camouflage protection against all detection systems that might reasonably be used against individual troops. It should be clear, for example, that a uniform so designed that it significantly reduces the probability of detection by infrared devices is useless, if its visual camouflage capabilities are thereby destroyed.

One vexing problem of this type has been the reconciling into a single clothing system of all the requirements for camouflage against visual, infrared photographic, and infrared-sensitive in the range 850 to 1200 nanometers. Photographic emulsions are available that are sensitive in the ultraviolet, visible and the near-infrared regions of the spectrum. The region of interest in this paper is that between about 750 and 900 nanometers, in which neither sniperscope system nor the eye are sensitive, but for which certain photographic emulsions have specifically been designed with enhanced sensitivity. Table I summarizes some of the more important ways in which a photographic surveillance system differs from the sniperscope and visual methods. Photographic observations are usually made in daylight from the air. Hence, the direction of viewing is predominantly vertical as compared with the predominantly horizontal viewing that is characteristic of the other two modes. Although visual observations are also made at night, most visual information is obtained in daylight. "Reaction time" reflects the fact that a period of time is required to make an exposure, process a film, and examine a final print. During the time required to react, some targets (e.g. troops) could easily move. The background against which an object is viewed from the air is essentially the solid ground. On the other hand, visual and sniperscope observations of an object are very often made against a background that is variable; some parts of the background may be near the object, some far behind it, and parts of the background may simply be void.

TABLE I Differences in Detection by Visual, Photographic and Sniperscope Systems as Usually Employed

	<u>Visual</u>	<u>Photographic</u>	<u>Sniperscope</u>
Wave length region (nanometers)	380 to 750	750 to 900	850 to 1200
Primary viewing	horizontal	vertical	horizontal
Primary use	daytime	daytime	nighttime
Reaction time	fast	slow	fast
Depth of background	deep	shallow	deep
Type of target for which effective	any	stationary	any
Ideal reflectance (%) for camouflage in wet climates	5 to 10	40 to 60	18 to 25

The differences summarized in Table I lead to an idealized reflectance curve for camouflage through the spectral region from 400 to 1200 nanometers. Figure 1 represents the spectral reflectance that a uniform should have in order to provide minimum contrast with the background, when it is viewed with any of the systems shown in Table I. The solid curve is one that would satisfy requirements for all conditions of viewing. The dashed curves that would afford adequate camouflage for day and for night. This assumes that the sniperscope would not be used in daylight and that photographic surveillance would be from the air in daylight, using infra-red-sensitive film.

Past efforts to develop a colorant formulation that would yield a reflectance curve such as the solid curve of Figure 1 have been unavailing. While it may be possible for a compound to absorb strongly at about 1000 nanometers and absorb only weakly at 850 nanometers, such behavior has only rarely been observed.⁽¹⁵⁾ The few specific organic compounds that have shown these characteristics have received limited attention due to their relatively poor fastness to light.⁽¹⁶⁾

It is, of course, unrealistic to consider using separate uniforms for day and night in order to obtain correspondence with the dashed curves of Figure 1. It is conceivable, however, that a fabric could be produced that would show different apparent reflectance characteristics, depending on the type of illumination that is used. This would be possible, if the fabric were to exhibit fluorescence in a band centering at about 850 nanometers,

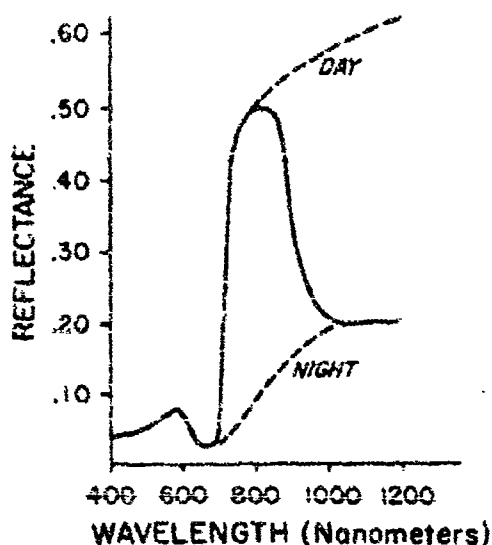


Figure 1. Idealized reflectance curve of a uniform fabric to afford camouflage protection over a spectral range from 400 to 1200 nanometers.

survey green and blue dyes were selected because they have absorption bands in the red part of the spectrum, and one would expect any fluorescence to appear in the near-infrared, the region of interest.

Secondly, the chemical structures have been reported⁽¹⁷⁾ for many dyes that are known to fluoresce in the visible spectrum. Green or blue dyes whose structures resemble rhodamine, fluorescein, etc., were therefore prime candidates for study.

It was also known that fluorescence is a source of difficulty and error in color measurement. When colorants are known to fluoresce, appropriate care can be taken to assure accuracy of the data. If, however, fluorescence appears in the infrared, being invisible, it may go unnoticed or unsuspected until serious delays or errors have occurred⁽¹⁸⁾. One dye was suggested by a colorist on the basis of just such an experience⁽¹⁹⁾.

As the preliminary results became available, a few dyes were observed to be fluorescent in the infrared. Green and blue dyes having related chemical structures were then included in the study. Relating the chemical structure and concentration of dyes and the influence of substrate to fluorescence are subjects of a continuing study that will be reported in a later paper.

thereby increasing the apparent reflectance in this region. While many dyes are known to fluoresce in the visible region of the spectrum, few references were found in the literature to dyes that fluoresce in the near-infrared.

2. Plan of Study

In order to test the concept, it was first necessary to find dyes that do fluoresce in the near-infrared. About 100 dyes were applied to various fabrics and examined with the photometer described in Section 4. Selection of dyes, however, was not random but based on certain known principles.

From Stokes' Law one expects to find an absorption band at wavelengths somewhat shorter than those that characterize the fluorescent emission. For example, rhodamine absorbs at about 550 nanometers and fluoresces at about 600 nanometers. Therefore, for this

3. Preparation and Dyeing of Fabric Samples

The ultimate objective of this study is a colorant system that exhibits infrared fluorescence when applied to fabric surfaces. For this reason, dyes were evaluated after being applied to fabric substrates rather than in solution. Initial emphasis was placed on cationic dyes, although many anionic dyes were subsequently studied.

a. Fabrics Chosen

- 1) Cloth, polyacrylic, oxford, 6.4 oz.
- 2) Cloth, cotton, lawn, 2.9 oz.
- 3) Cloth, polyamide, filament, twill, 1.6 oz.
- 4) Cloth, polyamide, filament, twill, 3 oz.
- 5) Cloth, polyamide, spun, 3 oz.
- 6) Cloth, viscose, banner, 5 oz.
- 7) Cloth, viscose, taffeta, 3 oz.
- 8) Cloth, acetate, taffeta, 3 oz.
- 9) Cloth, polyester, oxford, 3 oz.

b. Depth of Dyeings

Although the influence of concentration on degree of fluorescence is not considered in this paper, dyeings were made at three levels in preparation for that phase. Dyeings were based on stock solutions containing approximately 1 millimole per liter. The following aliquots were used for the three levels.

100 ml
50 ml
25 ml

All of the dyeings were made using swatches, 10g \pm 0.5g, of the various fabrics chosen. The fabric samples were in an already prepared condition and needed only to be wet out at 110°F with a non-ionic detergent. A liquor ratio of 40:1 was maintained for all of the dyeings. At the end of the dyeing cycle the samples were rinsed, dried and pressed. The dyed samples were then measured with a photometer for fluorescent emission. Results are reported only for the most effective concentration.

c. Dyeing Procedures

The following are the dyeing procedures used for the fabrics selected in this study. Stainless steel beakers were used in a constant temperature bath.

1) Cationic dyes on polyacrylic and viscose fabrics

The material was entered in a dyebath at 120°F made up with

the following components in demineralized water:

- 1% Sodium acetate
- 1% Acetic acid (56%)
- 1% Non-ionic surfactant (Caproacetyl Leveling Salt)
- 1% Organic cationic retarder (Retarder LAN)

The dyebath at pH of 5.0 was raised to the boil in 45 minutes. Boiling was continued for up to 2 hours or until the color had been removed from the dyebath. The fabric was removed and rinsed in demineralized water.

2) Direct dyes on cotton, polyamide and viscose fabrics

The dyeing was started at 110°F and the temperature raised to the boil in 30 minutes. The dye bath was boiled for 30 minutes longer. Anhydrous sodium sulfate was then added in portions to a total of 30 percent of the weight of fabric and boiling continued for 30 minutes. The dyeing was continued in a cooling bath for an additional 20 minutes, and the fabric rinsed in cold demineralized water for 5 minutes.

3) Acid dyes on polyamide fabrics

Acid dyes were applied to polyamide fabrics in a bath containing:

- 10% Anhydrous sodium sulfate
- 5% Ammonium acetate
- 3% Acetic acid (56%), to exhaust
- 1% Formic acid (90%), to exhaust

The dyeing was started at 120°F and the bath temperature gradually raised to 160°F and held at 160° ± 2°F for 30 minutes. Then the temperature was raised to the boil and dyeing continued at the boil for 1 hour with subsequent additions of acid in portions to promote exhaustion. Boiling was continued for an additional 15 minutes, after which the temperature was lowered and the fabric rinsed.

4) Mordant acid dyes on polyamide fabrics

Mordant dyes were applied to polyamide fabrics in a manner similar to acid dyes and after-chromed in a fresh bath with sodium dichromate and formic acid.

The material was entered at 85°F in a bath containing dissolved dye and 3% acetic acid (56%). The bath was raised to the boil in 30 minutes

and boiling continued for an additional 30 minutes. To exhaust the bath 4% formic acid (90%) was added and boiling was continued for 30 minutes longer.

Chrome development was accomplished by after-treatment in a fresh bath with:

1/4, 1/2, 1% Sodium dichromate (amounts equal to dye)
4% Formic acid (90%)

The bath temperature was raised to the boil and continued at the boil for 1 1/2 hours. The fabric was first rinsed thoroughly in hot water to remove unused sodium dichromate, then in warm and finally in cold water.

5) Special neutral dyeing colors on polyamide fabrics (super-nylite and Nylanthrene dyes)

The material was entered at 100°F in a dyebath containing:

4% Anhydrous sodium sulfate
4% Ammonium sulfate

The temperature was raised to 160°F in 30 minutes. The required salts were then added to the bath and the temperature raised to 180°F and the dyeing continued at 180° ± 2°F for 1 hour. The material was rinsed in warm and then in cold water.

6) Disperse dyes on acetate, polyamide and polyester fabrics

The dyestuffs were pasted with 1% anionic dispersant (Igepon T) in warm water before adding to the dyebath which was set at 120°F. The temperature was raised gradually to 200°F in 20 minutes and the dyeing continued at 200°- 205°F for 1 hour. The fabric was then rinsed in warm and cold water. Disperse dyes were applied on polyester fabric using a phenol derivative (Carolid) as a carrier. This was first dissolved in water and added to the dyebath to a concentration of 5 g/l and the pH was adjusted to 6.0. The bath was brought to a boil in 15 minutes and the boiling continued for 2 hours.

7) Reactive dyes on polyamide fabrics

The prepared material was entered in a dyebath at 100°F with 4% formic acid (90%) and the previously dissolved dyestuff. The rate of temperature rise of the dyebath was carefully controlled and brought to 205°F in 45 minutes, at which temperature the bath was maintained for 1 hour. The fabric was then rinsed in cold water and scoured for 10 minutes at 180° ± 5°F in 2 parts anionic surfactant (Igepon T) and 2 parts sodium carbonate per 1000 parts of water. The fabric was finally rinsed in cold water.

8) Solvent dyes on polyamide and polyacrylic fabrics

The solvent dye was first dissolved in 250 ml of methanol and then made into a 1-liter dispersion with water using 1.0 gram of anionic dispersant (Igepon T). A 10 gram sample of material was then dyed in 400 ml of the stock solution. The dye was applied in the same manner as a disperse dye at a low temperature of 120°-140°F for 1 hour. The fabric was thoroughly rinsed in warm water and then finally given a cold water rinse.

9) An additional investigation was made of direct dyes on both cotton and polyamide in both neutral and acid baths.

a) Neutral bath

The dyeing was started at 110°F and raised to the boil in 30 minutes. After continuing at the boil for 30 minutes, 30% anhydrous sodium sulfate was added and boiling continued for 30 minutes longer. The fabric then was finally given a cold rinse.

b) Acid bath

The material was added to the dye bath at 120°F which contained 10% anhydrous sodium sulfate and 5% ammonium acetate. The temperature was held for 15 minutes at 160°-180°F and then raised to the boil. Boiling was continued for 1 hour longer and the bath was finally exhausted with 1% acetic acid (56%).

4. Design of Fluorophotometer

The basic design of the fluorophotometer is shown in Figure 2. A sample at SP is illuminated normal to its surface by a collimated beam from a 150-watt, 6-volt tungsten lamp. This beam passes through a filter, F-1, that absorbs light at wavelengths longer than 700 nanometers. This filter is actually a combination of a heat absorbing filter and an interference filter in series.*

The detector, RCA-917, is placed at 45° to the normal. Two Corning 2600 filters are placed in front of the detector (F-2). This combination absorbs radiation at wavelengths shorter than 700 nanometers.

The transmittance of F-2, a nominal sensitivity of the detector, and their product are shown in Figure 3. The transmittance of the two components and their combination that were used for F-1 are shown in Figure 4.

*Heat absorbing filter - KQ3 (thin)

Interference filter - No. 648

Both obtained from Optics Technology, Inc., Palo Alto, California.

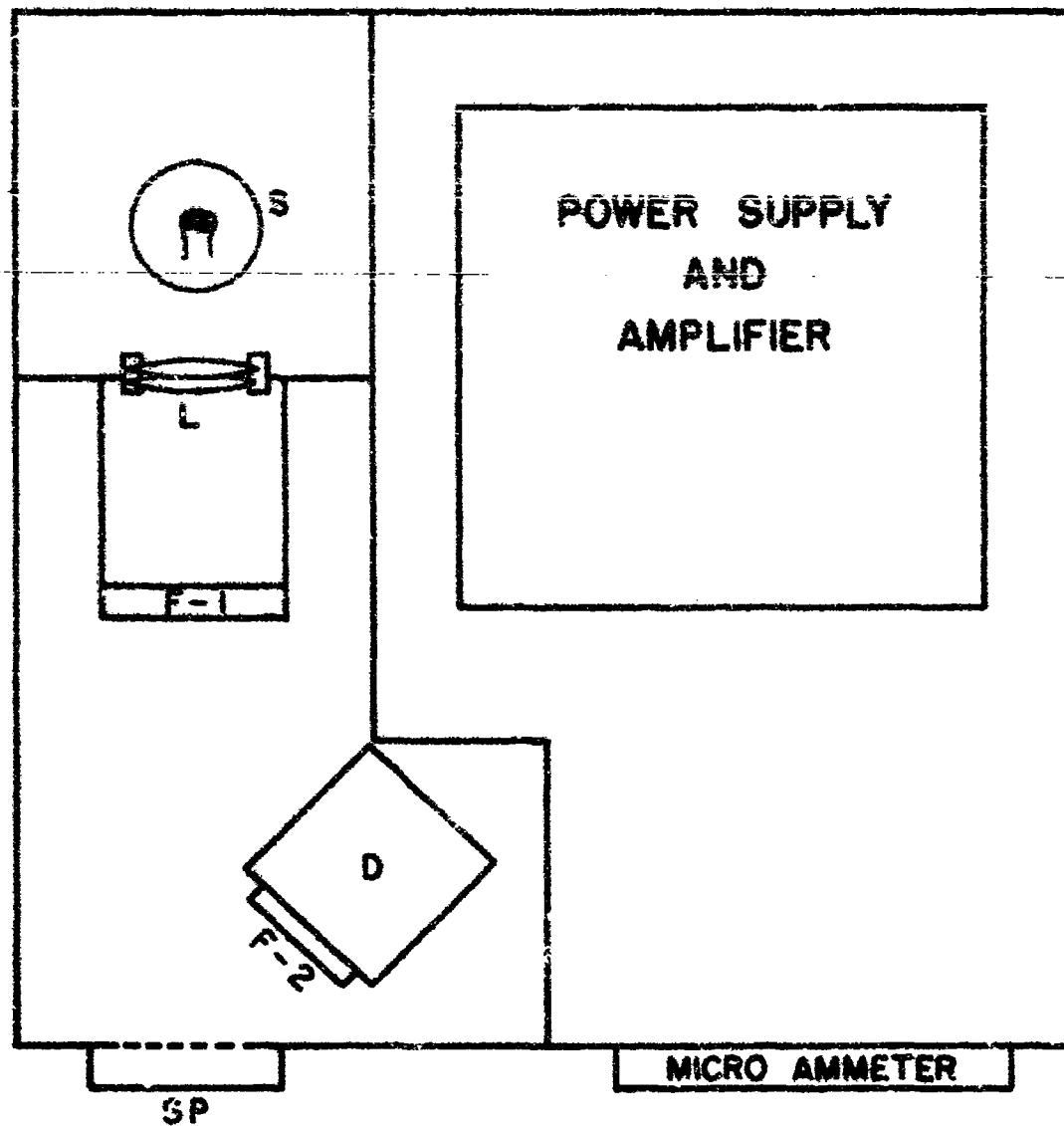


Figure 2. Schematic Diagram of Infrared Fluorophotometer.

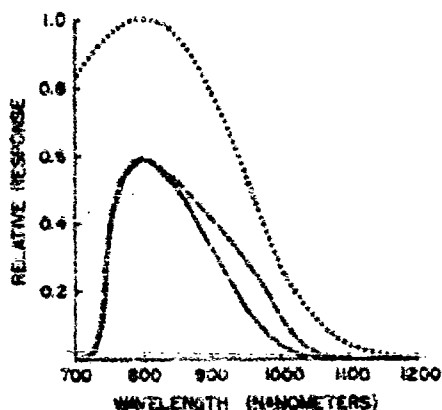


Figure 3. Transmittance of F-2 (dashed line), a nominal sensitivity of the detector (dotted line), and their product (solid line).

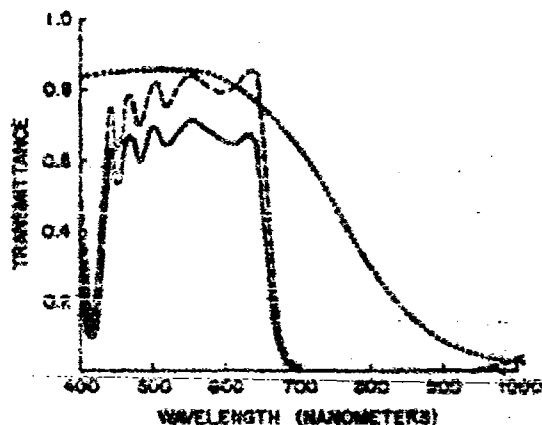


Figure 4. Transmittance of combined F-1 filter - solid line; and components, heat absorbing filter - dotted line; and interference filter - dashed line.

The instrument was balanced to read zero with the specimen holder alone in the sample port. The holder is blackened with a paint containing carbon black and has a reflectance of less than 4 percent. When an undyed, white fabric is placed in the sample position, a reading of about 8 microamperes is obtained. This probably represents the degree of overlap in the transmittances of the filters F-1 and F-2. Readings less than 10 microamperes are considered to indicate the absence of fluorescence in the range of the spectrum defined by the instrument.

5. Fluorophotometer Measurements

Table II lists those dyes, applied to the indicated substrates, for which readings of less than 10 microamperes were observed. These samples are considered not to fluoresce in the infrared.

Table III lists those samples for which readings of between 10 and 15 microamperes were obtained. These are regarded as weakly or doubtfully fluorescent.

Samples listed in Table IV are those for which values were observed between 15 and 30 microamperes. These are regarded as moderately fluorescent.

Tables V and VI list those dyes that are regarded as strongly fluorescent in the infrared. Samples for which readings between 30 and 50 microamperes were obtained are shown in Table V; those for which readings of above 50 were obtained are given in Table VI. A few of these dyes are listed in more than one table, when applied to more than one fiber with different results.

TABLE II: Dyes that do not fluoresce in the near infrared

<u>Dye</u>	<u>C.I. Number</u>	<u>Chemical Type</u>	<u>Substrate</u>
*Basic Blue 3	51005	oxazine	cotton
*Basic Blue 4	51004	oxazine	cotton
Basic Blue 5	42140	triarylmethane	rayon
Basic Blue 40	none	not known	polyacrylic
Basic Green 6	none	quinoline	polyacrylic
Basic Violet 18	none	monoazo	polyacrylic
Acid Blue 40	62125	anthraquinone	polyamide
Acid Blue 185	none	phthalocyanine	polyamide
Acid Green 1	10020	quinoneoxime	polyamide
Acid Black 24	26370	trisazo	polyamide
Mordant Blue 1	43830	triarylmethane	polyamide
Mordant Blue 3	43820	triarylmethane	polyamide
Mordant Blue 10	51030	oxazine	polyamide
Mordant Blue 19	none	monoazo	polyamide
Mordant Blue 45	51045	oxazine	polyamide
Mordant Blue 56	51120	oxazine	polyamide
Mordant Green 4	10005	quinoneoxime	polyamide
Mordant Green 22	45510	phthalein	polyamide
Mordant Black 3	14640	monoazo	polyamide
Mordant Black 11	14645	monoazo	polyamide
Direct Blue 24	none	trisazo	cotton
Direct Blue 40	none	disazo	cotton
Direct Blue 67	27925	disazo	cotton
Direct Blue 71	34140	trisazo	cotton
Direct Blue 75	34220	trisazo	cotton
Direct Blue 76	24410	disazo (metal)	cotton
Direct Blue 78	34200	trisazo	cotton
Direct Blue 80	none	disazo (metal)	cotton
Direct Blue 81	34215	trisazo	cotton
Direct Blue 86	74180	phthalocyanine	polyamide
Direct Blue 87	74200	phthalocyanine	cotton
Direct Blue 98	23155	disazo (metal)	cotton
Direct Blue 207	none	disazo	cotton
Direct Green 1	30280	trisazo	cotton
Direct Green 6	30295	trisazo	polyamide
Direct Green 8	30315	trisazo	cotton
Direct Green 12	30290	trisazo	cotton
Direct Green 15	none	trisazo	polyamide
Direct Green 26	34045	trisazo	cotton
Direct Green 27	none	polyazo	polyamide

*Mordanted with tannin

TABLE II (Cont'd)

<u>Dye</u>	<u>C.I. Number</u>	<u>Chemical Type</u>	<u>Substrate</u>
Direct Green 28	14155	monazo	polyamide
Direct Green 35	none	trisazo	cotton
Direct Green 37	none	trisazo	cotton
Direct Green 65	none	monazo	cotton
Direct Green 66	none	trisazo	cotton
Reactive Blue 3	none	phthalocyanine	polyamide
Reactive Blue 25	none	not known	polyamide
Disperse Blue 72	none	anthraquinone	polyester
Solvent Blue 25	74350	phthalocyanine	polyacrylic
Ingrain Blue 1	74240	phthalocyanine	polyamide
Brilliant Cresyl Blue	51010	oxazine	polyacrylic
Pigment Green 8	10006	quinoneoxime	cotton
Basacryl Blue 214	none	not known	polyacrylic
Basacryl Blue Violet 507	none	not known	polyacrylic
Amichrome Light Navy RBLL	none	not known	polyamide
Amichrome Brilliant Green 2JL	none	not known	polyamide
Amichrome Light Deep Green JLL	none	not known	polyamide
Astrazon Olive Green BL	none	not known	polyacrylic
Levalan Navy Blue IRL	none	not known	polyamide
Chromindigen Blue BRA	none	not known	polyamide
Nylanthrene Green 2GFL	none	not known	polyamide
Verofix Brilliant Blue 3GL	none	not known	polyamide
Acid Brilliant Blue DHH	none	not known	polyamide
Wool Green 2442	none	not known	polyamide
Wool Fast Turquoise Blue SW	none	not known	polyamide
Resoline Blue RRL	none	not known	polyester
Chlorantine Fast Blue 3FLL	none	not known	cotton
Chlorantine Fast Blue 4GLD	none	not known	cotton
Chlorantine Fast Blue 8GLL	none	not known	cotton
Chlorantine Fast Blue 9GLL	none	not known	cotton
Direct Fast Green 2GL	none	not known	cotton

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TABLE IV: Dyes that fluoresce moderately in the infrared

<u>Dye</u>	<u>C.I. No.</u>	<u>Chemical Type</u>	<u>Fabric</u>	<u>Instrument Reading</u>
Basic Blue 1	42025	triarylmethane	polyacrylic	28
Basic Blue 5	42140	triarylmethane	polyacrylic	30
Basic Blue 6	51175	oxazine	polyacrylic	22
Basic Blue 11	44040	triarylmethane	polyacrylic	30
Basic Green 4	42000	triarylmethane	polyacrylic	28
Disperse Blue 71	none	anthraquinone	polyamide	22
Acridine Red	45000	xanthene	polyacrylic	23
Acid Blue 93	42780	triarylmethane	polyamide	20
Direct Blue 6	22610	disazo	cotton	30
Direct Blue 21	23710	disazo	cotton	26
Direct Blue 106	51300	oxazine	cotton	25
Direct Blue 107	51315	oxazine	cotton	20
Direct Blue 108	51320	oxazine	cotton	30
Genacyl Blue 5G	none	not known	polyacrylic	26

TABLE V: Dyes that fluoresce strongly in the infrared

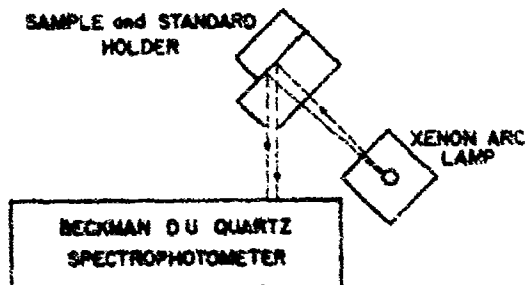
<u>Dye</u>	<u>C.I. No.</u>	<u>Chemical Type</u>	<u>Fabric</u>	<u>Instrument Reading</u>
Basic Blue 7	42595	triarylmethane	polyacrylic	32
Basic Blue 9	52015	thiazine	rayon	32
Basic Blue 26	44045	triarylmethane	polyacrylic	45
Basic Blue 36	none	triarylmethane	polyacrylic	42
Basic Green 1	42040	triarylmethane	polyacrylic	37
Basic Green 3	none	triarylmethane	polyacrylic	45
Basic Violet 3	42555	triarylmethane	polyacrylic	37
Basic Violet 4	42600	triarylmethane	polyacrylic	48
Basic Violet 5	50205	azine	polyacrylic	33
Acid Green 3	42085	triarylmethane	polyamide	40
Acid Green 16	44025	triarylmethane	polyamide	41
Direct Blue 1	24410	disazo	cotton	42
Direct Blue 14	23850	disazo	cotton	36
Direct Blue 22	24280	disazo	cotton	32
Direct Blue 25	23790	disazo	cotton	37
Direct Blue 109	51310	oxazine	cotton	35

TABLE VI: Dyes that fluoresce very strongly in the infrared

<u>Dye</u>	<u>C.I. No.</u>	<u>Chemical Type</u>		<u>Instrument Reading</u>
Basic Blue 3	51005	oxazine	polyacrylic	155
Basic Blue 4	51004	oxazine	polyacrylic	160
Basic Blue 9	52015	thiazine	polyacrylic	62
Direct Blue 106	51300	oxazine	polyamide	82
Direct Blue 107	51315	oxazine	polyamide	68
Direct Blue 108	51320	oxazine	polyamide	96
Direct Blue 109	51310	oxazine	polyamide	72
Direct Violet 54	51325	oxazine	polyamide	63

6. Spectrophotometric Measurements

Measurements of spectral radiance relative to that of magnesium carbonate were made for several samples of interest, using a "reverse optics" arrangement⁽²⁰⁾. Fabric samples were first illuminated with the full spectral emission of a 150-watt xenon high-pressure arc lamp. The reflected and fluoresced radiation was then analyzed by the monochromator of a Beckman DU spectrophotometer. This is shown schematically in Figure 5.



Four dyes were chosen for this more detailed spectrophotometric analysis as shown in Table VII. One of the samples (Brilliant Cresyl Blue) was found with the fluorophotometer to be not fluorescent; the other three were fluorescent in varying degrees as shown by the instrument reading. All four dyes are oxazines.

Figure 5. Reverse optics arrangement of Beckman DU spectrophotometer for measurement of fluorescent fabrics.

TABLE VII: Description of samples on which spectrophotometric measurements were made

<u>Dye</u>	<u>C.I. No.</u>	<u>Fabric</u>	<u>Reading</u>
Brilliant Cresyl Blue	51010	polyacrylic	7
Direct Blue 106	51300	polyamide	82
Direct Blue 108	51320	polyamide	96
Basic Blue 4	51004	polyacrylic	160

The results of the spectrophotometric measurements are shown in Figures 6 and 7. The curve for Brilliant Cresyl Blue (non-fluorescent) appears, for comparison, in both figures. It is apparent from these figures that the greater the instrument reading (i.e., infrared fluorescence) the greater is the difference in curves with respect to that for Brilliant Cresyl Blue in the region beyond 700 nanometers.

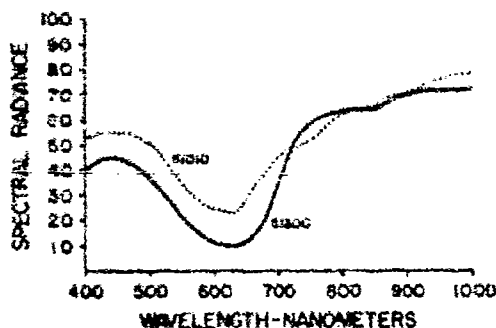


Figure 6. Spectral radiance of Brilliant Cresyl Blue (non-fluorescent) - on polyacrylic fabric - dotted line; and Direct Blue 106 (fluorescent on polyamide fabric) - solid line.

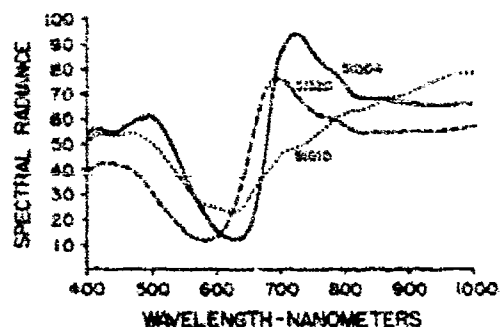


Figure 7. Spectral radiance of Brilliant Cresyl Blue (non-fluorescent) - dotted line; and Basic Blue 4 (fluorescent) - solid line; both on polyacrylic fabric; and Direct Blue 108 (fluorescent) on polyamide fabric - dashed line.

7. Conclusions

Over 125 dyes were examined for fluorescence in the infrared with a fluorophotometer designed for this purpose. Of these, about half showed no evidence of fluorescence beyond 700 nanometers, and about one quarter produced only a feeble response. However, 36 of the dyes examined were fluorescent in the infrared to a degree sufficient to warrant further study.

Oxazines were the most fluorescent of the types studied. Other similar structures, however, such as thiazines, xanthenes, azines, and triarylmethanes were only somewhat less effective. On the other hand, hydroxy-oxazines and the related oxazones were found to be not fluorescent.

These studies are continuing with emphasis on three factors that appear to influence fluorescence.

a. It is clear that substituent groups influence the wavelength and intensity of absorption bands. It is reasonable to suppose that fluorescence will also be influenced by chemical structure.

b. The fluorescence appears to be influenced markedly by the type of fiber to which the dye is applied. For example, when Basic Blue 4 was mordanted with tannin to cotton, no fluorescence was observed. When applied to a polyacrylic fabric, the same dye produced a very strong fluorescence.

c. It is well known that the degree of fluorescence often increases with concentration until a maximum is reached. Increasing the concentration above that point results in a decreased fluorescence, a phenomenon referred to as self-quenching.

These are the principal areas of further study for which only qualitative evidence is now available.

8. References

1. Gee, D. L. and Humphreys, A. H., User review of camouflage for the individual combat soldier in the field, Report 1834, U. S. Army Engineer Research and Development Laboratories, Ft. Belvoir, Va., (Oct. 1965).
2. Anon. Hand-Held radar. Mil. Rev., 44, 99 (May 1964).
3. French, R. H., Assembly design of miniature lightweight hand-held radar set AN/PPS-6. Tech. Rpt. 2421, U. S. Army Electronics R&D Labs, Ft. Monmouth, N. J. (Sept. 1963) AD604479.
4. Anon., Night Vision device, Mil. Rev., 45, 104 (Jan. 1965).
5. Aufderheide, M. B. and N. Dougherty, Image amplifier laboratory evaluation program, Tech. Doc. Rpt., AL TDR 64-211, Air Force Systems Com., Wright-Patterson AF Base, Ohio (19 Oct. 1964) AD609945.
6. Gebel, R., Light amplification and its importance in modern warfare. WADC Tech. Note 57-318, Air R&D Com., Wright-Patterson AF Base, Ohio (Sep. 1957) AD131047.
7. Anon., Infrared image tube, Electronics, p. 112 (Sep. 1964).
8. Pratt, T. H., An infrared image-converter tube, J. Sci. Inst., 24, 12 (Dec. 1947).
9. Welti, A. and P. Schranz, Night vision with an infrared image converter, Albiswerk-Berichte, 10, 10-24 (July 1950) English trans. AD610765.

10. Astheimer, R. W. and E. M. Wormser, *J. Opt. Soc. Amer.*, 49, 179-87 (1959).
11. Iyancov, Y. A. and B. V. Tyapkin, *Infrared technology in military matters*, Izdatel'stov "Sovetskoe Radio", Moscow, 1963, English Trans. AD610765.
12. Anon., Soviet evapographic chamber to represent remotely the infrared zone of the spectrum, *J. Mechanika A Optika* (Czech), No. 10, 325 (1963), English trans. AD457869.
13. Grabe, B., A survey of infrared technology, Tech. Rpt., 64-29, Swedish Defense Lab (Nov. 1964) English trans. AD461402.
14. Anon., Evaluation of thermograph T-3, U. S. Army Infantry Bd., Ft. Benning, Ga. (Jan. 1963).
15. Calco Chemical Company (American Cyanamid), Developing dye and pigment formulations, Contract Nos. DA44-109-gm-811 and DA44-109-gm-2081, Philadelphia QM Depot, 1950 through 1953.
16. Rizzo, F. J., B. A. Natsios and A. O. Ramsley, Absorbers of near infrared radiation, *Mat. Res. and Eng. Rpt. No. 64-10*, U. S. Army Natick Laboratories, Natick, Mass. (June 1964).
17. *Colour Index*, 2nd 1956, Soc. Dyers and Colourists and Am. Assoc. Tex. Chemists and Colorists.
18. Ramsley, A. O., Fluorescence of dyes in the infrared, *Color Engineering*, (in press).
19. Davidson, H. R., private communication to the authors.
20. Judd, D. B. and Wyszecki, G., Color in Business, Science and Industry, 2nd ed., Wiley, 1961.

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13. ABSTRACT <p>Camouflage against visual observation or detection by infrared image-converters requires that the reflectance of objects be relatively low. On the other hand, camouflage against infrared-sensitive photography requires that reflectance in the appropriate spectral region be relatively high. Reasons for these restrictions are discussed.</p> <p>Of possible approaches to attain desired reflectance characteristics, that involving fluorescence in the near infrared is discussed. A methodology for searching for suitable dyes and the design of an instrument that can identify the invisible infrared fluorescence are described. The infrared fluorescence characteristics of over 100 dyes applied to various fabrics is given.</p>		

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