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APPLICATION OF INFRARED ABSORBERS TO NYLON 6,6

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In an attempt to provide a method of achieving near infrared camouflage with textiles having wide military applicability, proprietary infrared absorbers (aminium radical cation type) IR-99 and IR-117 were applied to Nylon 6,6. Pre-dyeing the nylon with an acid dye, or pre-treating it with certain organic salts increased the uptake of infrared absorber, but light stability was poor in all cases. Further work utilizing this approach does not appear warranted until infrared absorbers having better lightfastness characteristics are available.

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FOREWORD

The feasibility of providing personal camouflage against devices operating in the near infrared region of the spectrum has been demonstrated by previous work at Natick Laboratories, using dyes which fluoresce in the infrared. The present work was directed at obtaining similar spectral characteristics on a commonly used military fabric.

The present work was suggested by an Unsolicited Proposal from American Cyanamid. The program was directed by the Flame and Thermal Protection Section, Chemical Modification of Textiles Branch, Textile Research and Engineering Division of the Clothing and Personal Life Support Equipment Laboratory. Project Officer was Mr. A. O. Ramsley with Dr. E. M. Healy as alternate.

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ABSTRACT

In an attempt to provide a method of achieving near infrared camouflage with textiles having wide military applicability, proprietary infrared absorbers (aminium radical cation type) IR-99 and IR-117 were applied to Nylon 6,6. Pre-dyeing the nylon with an acid dye, or pretreating it with certain organic salts increased the uptake of infrared absorber, but light stability was poor in all cases. Further work utilizing this approach does not appear warranted until infrared absorbers having better lightfastness characteristics are available.

A. Introduction

In his report, "Modern Counter-Surveillance in Combat Clothing", (1) Ramsley develops the idealized reflectance curve (Fig. 1) for camouflage in typical vegetated terrains. The camouflage is intended against such surveillance devices, as the eye and photography in the visible region, and the sniperscope, the image intensifier and infrared photography in the near infrared region. The notable property of the idealized reflectance curve is the maximum between 700 and 900 nanometers.

Infrared absorbing vat dyes have been used to produce low infrared reflectance, but they do not have the required reflectance maximum. A few dyes such as Acid Blue 158 (see appendix and figure 2), have weak infrared absorption and therefore a shallow reflectance maximum between 700 and 900 nanometers. However, their infrared reflectance is firmly fixed relative to the visible reflectance; therefore, there is no latitude for adjusting the visible shade to lighter tones while holding a low infrared reflectance.

A reflectance curve having the general shape of the idealized reflectance curve has been obtained by Ramsley (1) from a fabric made by interweaving into a fabric dyed with an infrared fluorescing dye some black carbon-pigmented fibers. This special construction was necessary to prevent quenching of the infrared fluorescence which is necessary to attain the maximum in the infrared portion of the response curve.

Certain infrared absorbing aminium radical-cations (3,4), greenish in color, have absorption maxima above 900 nanometers. In combination with a blue or green dye they will yield a reflectance spectrum with a peak between 700 and 900 nanometers. Previously these compounds have been applied to cotton and nylon by padding with a resin-emulsion or with an acetone solution (5). Although the treated cloth samples had considerable infrared absorption, the lightfastness was poor, failing badly after 20 hours in a Fadeometer.

Since true dyeings are equilibrium situations that are reproducible, then the aminium radical-cation infrared absorber should behave like basic or cationic dyes. This they do, as it was found that they exhaust well onto acrylic fibers and also Nylon 844, a nylon having built-in anionic groups. During the dyeing process, cationic dyes diffuse to the anion sites in the acrylic fibers or nylon 844, where they are held by electrostatic attraction. However, the fabrics of choice for military clothing are nylon 6,6/cotton blends which are not normally dyeable with cationic dyes.
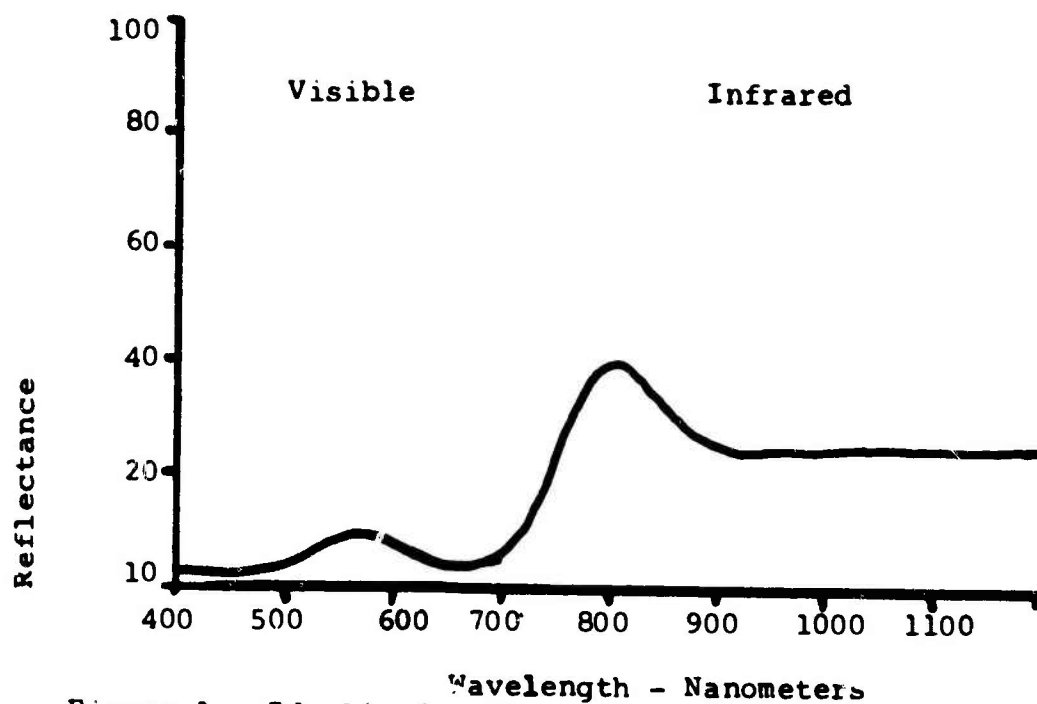
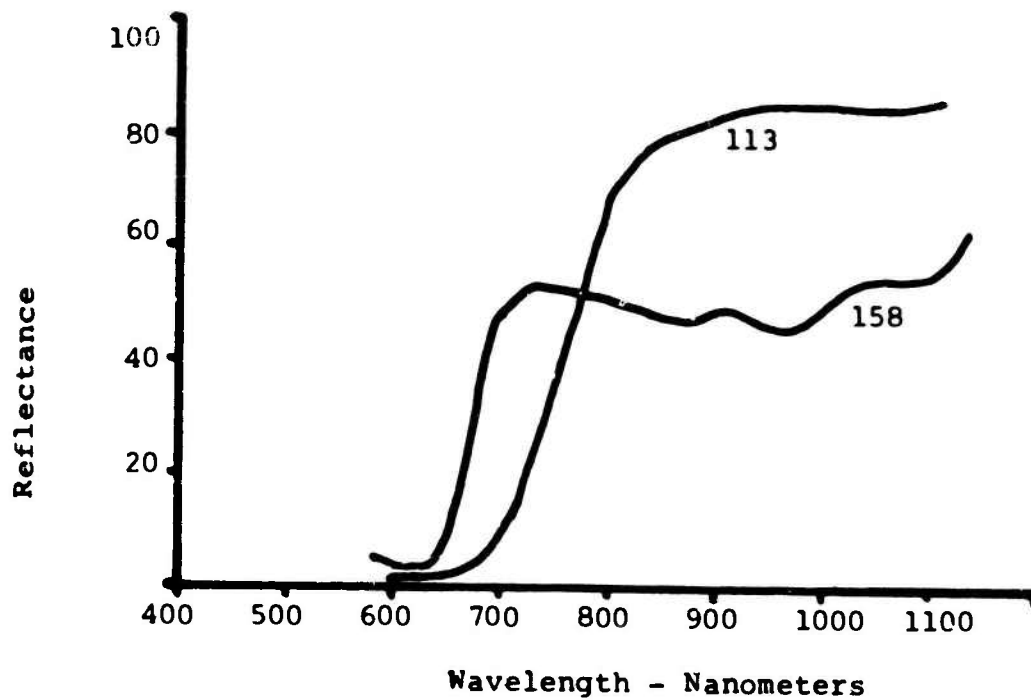Figure 1 - Idealized reflectance curve for camouflage in typical vegetated terrains

Figure 2 - Reflectance curves of an infrared absorbing dye (Acid Blue 158) and an infrared transmitting dye (Acid Blue 113) on nylon 6,6

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B. Scope of Work

The first goal of this project was to find a suitable method to dye infrared absorbers on nylon, as nylon is the major constituent for most military nylon-cotton blends. Experiments studying the effect of pH, the effect of organic salts and the effect of acid dyes (previously dyed on the nylon) were made.

Secondly, the light stabilities of acceptable dyeings of infrared absorber IR 99 were measured under UV and IR filters so that the relative effects of ultraviolet, visible and infrared radiation could be determined.

Finally, two mixtures of dyes and infrared absorber IR 99 were dyed on nylon in an initial attempt to indicate the feasibility of color matching of military colors.

C. Experimental

The materials used included Cyasorb® IR 99 Light Absorber, Cyasorb® IR 117 Light Absorber, and several acid dyes, all obtained from the American Cyanamid Company. Structures are given in Appendix II. The alkali salts of citric, phthalic, fumaric acids and of saccharin were obtained from laboratory supply houses. Dyeings were carried out on spun nylon; Type 200 fabric, Testfabrics, Inc., Style #358, Lot 5045.

The equipment for the dyeings were standard laboratory dyeing apparatus. Light exposure studies were made using the Atlas carbon arc Fadeometer, and spectral data were obtained with Beckman DK-2 and General Electric-Hardy spectrophotometers.

The dyeing procedures, Appendix III, all utilized 40:1 liquor-cloth ratios at boiling temperatures. The infrared absorbers were applied at 0.2 or 0.25 percent, based on weight of fabric.

Dyeings of infrared absorber IR 99 and IR 117 require that they be well dispersed. An effective method is to pour an acetone solution of the absorber into water containing a non-ionic surfactant (Appendix III).

Four dyeings of IR 99 and IR 117 in non-buffered, non-salted dyebaths at pH's 3,5,7 and 9, (Table I and II) established a reference point for dyeings with salts and buffers. These pH's were adjusted by acetic acid or ammonia.

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Table I

Reflectance of Cyasorb IR 99 Absorbers on Nylon

Sample No.	Dyeing Conditions 0.2% IR Absorber	@ 960 nm %R	Fr(a)
1	Undyed nylon-no IR Absorber	(87.5)	(0.01)
2	Unbuffered, pH 3	41.6	0.41
3	Unbuffered, pH 5	44.7	0.34
4	Unbuffered, pH 7	40.3	0.44
5	Unbuffered, pH 9	40.1	0.45
6	With 20.0% KH phthalate pH 5.0	77.0	0.03
7	With 20.0% Na saccharin pH 5.4	21.9	1.39
8	0.5% UV 284 (b)	30.6	0.79
9	0.5% Na saccharin (b)	32.9	0.68
10	0.5% Na fumarate (b)	32.9	0.68
11	0.5% K citrate (b)	36.6	0.55
12	0.5% KH phthalate (b)	35.9	0.57
13	5.0% K citrate (b)	41.6	0.41
14	1.0% Acid Yellow 54 (c)	23.0	1.29
15	" " "	24.0	1.20
16	1.0% Acid Yellow 9 (c)	26.8	1.00
17	" " "	24.5	1.16
18	1.0% Acid Yellow 23 (c)	26.4	1.03
19	" " "	27.3	0.97
20	1.0% Acid Yellow 17 (c)	24.0	1.20
21	" " "	18.5	1.80
22	1.0% Acid Yellow 34 (c)	23.5	1.24
23	" " "	20.4	1.55
24	1.0% Acid Green 41 (c)	26.0	1.05
25	" " "	25.6	1.08
26	1.0% Acid Blue 113 (c)	14.6	2.50
27	" " "	14.7	2.48
28	1.0% Acid Blue 158 (c)	(23.7)	(1.23)
28	" " " % IR Absorber (calc.)	28.0	0.93
29	1.0% Acid Blue 158 (c)	(22.7)	(1.32)
29	" " " % IR Absorber (calc.)	26.5	1.02
30	1.0% Acid Blue 150 No IR Absorber	(46.7)	(0.30)

All percentages based on weight of Fiber
(a)   Fr are Kubelka - Munk K/S values
(b)   Pretreatments of these salts made at pH 3.5, followed by dyeing of IR Absorber at pH 6.5
(c)   Nylon predyed with the acid dye; IR Absorber dyed at pH 6.5

Table II

Reflectance of Cyasorb IR-117 Absorber on Nylon

Sample No.	Dyeing with 0.2% IR Absorber	@ 900 nm %R	Fr(a)
1	Undyed nylon-no IR Absorber	(87.5)	(0.01)
31	Unbuffered, pH 3	65.5	0.09
32	Unbuffered, pH 5	61.6	0.12
33	Unbuffered, pH 7	63.1	0.11
34	Unbuffered, pH 9	58.1	0.15
35	1.0% Acid Yellow 54 (b)	76.9	0.03
36	1.0% Acid Yellow 9 (b)	72.8	0.05
37	1.0% Acid Yellow 23 (b)	70.4	0.06
38	1.0% Acid Yellow 17 (b)	71.8	0.06
39	1.0% Acid Yellow 34 (b)	71.2	0.06
40	1.0% Acid Green 41 (b)	71.7	0.06
41	1.0% Acid Blue 113 (b)	62.8	0.11
42	1.0% Acid Blue 158 (b)	(46.4)	(0.31)
42	" " "%R of IR Absorber(calc)	86.0	0.01
30	1.0% Acid Blue 158-no IR Absorber	(46.7)	(0.30)

All percentages are based on weight of Fiber

(a)　　Fr are Kubelka - Munk K/S values
(b)　　Nylon predyed with the acid dye; IR Absorber dyed at pH 6.5

The effect of high concentrations of salts on the dyeing of nylon with 0.2% (o.w.f.) of IR 99 was demonstrated with dye baths containing 20% on weight of fiber (5 grams per liter) of potassium acid phthalate and 20% of sodium salt of saccharin respectively, and at their natural pH's of 5.0 and 5.4 (Table I, samples 6 and 7).

The effect of smaller concentrations of salts on the dyeing of nylon with IR 99 utilized the above two salts as well as salts of fumaric acid, citric acid, and 2-hydroxybenzophenone-4-sulfonic acid (an ultraviolet light absorber). In this set of dyeings, the nylon was first treated with 0.5% (o.w.f.) of these salts in boiling aqueous baths at pH 3.5 for 1 hour, then, raising the pH to 6.5 and adding the IR 99, the final dyeing was carried out for 1 hour at the boil (Table I, samples 8-13).

Eight acid dyes, Appendix II, structures 3 through 10, were selected, first, for the presence of one or two sulfonate groups; second, for their good light stability; third, as examples of different chemical types as azo (#4), bisazo (#9), metallized azo (#10), azopyrazolone (# 5,6,7), metallized azopyrazolone (#3), and anthraquinone (#8); fourth, as examples of different colors such as yellow, green and blue; and fifth, as examples of small variations within one chemical type, e.g. structures 5,6 and 7 in Appendix II, are phenylazopyrazolones, some with chloro or carboxy groups.

These acid dyes were dyed on nylon at 1.0% on weight of fiber by normal procedures, Appendix III. It was calculated that 1.0% dyeings would provide 0.002 to 0.003 equivalents of sulfonate groups per 100 grams of dyed nylon. Thus there are enough anionic sites theoretically to b 1.4% of IR 99 or 1.8% IR 117. In a subsequent separate step, 0.2% of IR 99 and IR 117 were dyed at pH 6.5 on these acid-dyed samples. The dye baths for IR 99 visually appeared to be well exhausted, and some of these baths were analyzed spectrophotometrically for IR 99 (Table III). The reflectance readings of IR 99 at 960 nm on nylon fabric are reported in Table I, samples 14 through 29 and the reflectance of IR 117 at 900 nm on nylon fabric are listed in Table II, samples 35 through 42. Since acid blue 158 had its own absorption bands at 960 and 900 nanometers, it's contribution to the infrared absorption in samples 28, 29 and 42 was subtracted, leaving calculated reflectance values for IR 99 and IR 117.

For testing light stability, small pieces of nylon samples dyed with infrared absorbers were mounted on cardboard and exposed in a Fadeometer. From infrared reflectance readings before and after exposures, the percentage of remaining infrared absorber is easily calculated from the Kubelka-Munk K/S or Fr values (Appendix I). The reflectances were measured on the pieces of cloth doubled in thickness to minimize the white cardboard background.

In order to compare the effects of ultraviolet, visible and near infrared radiation on the infrared absorber, one third of the mounted sample was covered with a plastic ultraviolet absorbing screen having a fifty percent cut-off at about 420 nm. Another third

Table III

Efficiency of Dyeing of IR 99 on Nylon

Sample	(1) Absorbance	% Left In Bath	%R @ 960nm	(2) $(Fr)t$	(3) a_r
14 Yellow 54	.629	12.7	23.0	1.29	7.4
16 Yellow 9	.370	7.6	26.8	1.00	5.4
18 Yellow 23	.161	3.3	26.4	1.03	5.3
20 Yellow 17	.319	6.5	24.0	1.20	6.4
22 Yellow 34	.175	3.5	23.5	1.24	6.4
24 Green 41	.361	7.4	26.0	1.05	5.6
26 Blue 113	.133	2.7	14.5	2.52	12.9
28 Blue 158	.721	14.7	28.0[4]	.93	5.5
Starting Bath	4.875	100.0	-	-	-

(1) Spectrophotometric determination of absorbance

(2) Kubelka-Munk function - see reference 2 and Appendix I

(3) a_r = dyeing absorbency index - see Appendix I

(4) % R @ 960 nm due to IR 99 only

was covered with a dark red glass filter (Schott RG 665, 3 mm thick) having a 50% cut-off at 665 nm. The final third had either no filter or a plain clear glass plate (92% transmittance). To summarize, these filters have the following effects:

(1) clear glass-transmits UV, visible and IR
(2) UV screen-transmits visible and IR
(3) Red filter-transmits IR only

The results are given in Table IV. Since good data is obtained only from suitable dyeings, data from very light dyeings was not procured.

Two preliminary dyeings to approximate the shades of OG 107 and Tan 337 were attempted. The formulas were estimated from available reflectance data of some commercial acid dyes on nylon.

OG 107 - with IR
0.78% Acid Green 41
0.23% Acid Orange 69
0.06% Acid Red 151
0.25% IR 99

Table IV

Effect of Exposure of IR 99 on Nylon Behind Filters in Fadeometers

Sample No.	Dyeing Conditions	% IR 99 Remaining After 5Hrs. Filter			
		None	Glass	UV abs.	IR pass
5	pH 9	56	–	96	98
7	pH 5.4 20% saccharin	36	–	65	95
8	pH 6.5 0.5% UV 284	62	–	77	92
9	pH 6.5 0.5% saccharin	77	–	74	103
10	pH 6.5 0.5% fumarate	69	–	78	96
11	pH 6.5 0.5% citrate	114	–	80	94
12	pH 6.5 0.5% phthalate	90	–	72	107
13	pH 6.5 5% citrate	69	–	78	95
14	pH 6.5 on Yellow 54	24	39	65	90
16	pH 6.5 on Yellow 9	34	35	70	94
18	pH 6.5 on Yellow 23	26	38	77	114
20	pH 6.5 on Yellow 17	42	52	75	86
22	pH 6.5 on Yellow 34	30	37	61	106
24	pH 6.5 on Green 41	33	26	65	61
26	pH 6.5 on Blue 113	27	31	65	86
28	pH 6.5 on Blue 158	21	46	68	92
	Average	51	(55)a	73	94
	Average 14-28	30	38	68	91

(a) Estimated from average in "None" column

    Tan 337 - with IR
    0.05% Acid Green 41
    0.03% Acid Blue 25
    0.025% Acid Red 151
    0.03% Acid Orange 69
    0.07% Acid Yellow 17
    0.25% IR 99

The reflectance curves, figures 3 and 4, show that the dyeings have the approximate spectral shapes but are quite weak. The computer color match program gives the following analyses of OG 107 and Tan 337 samples and the above.
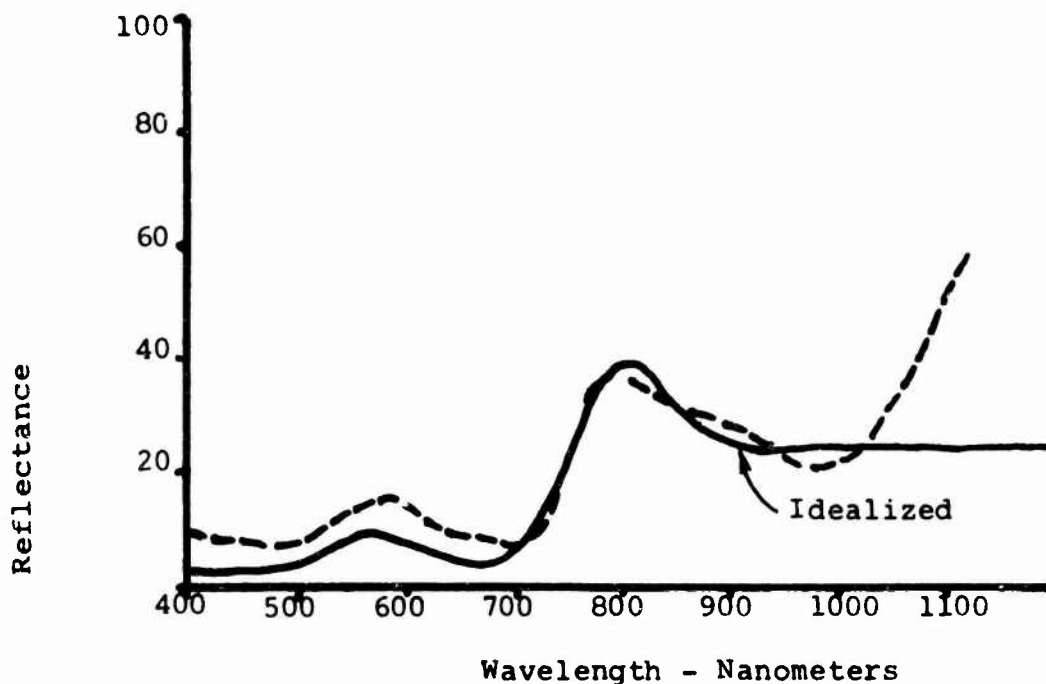
Figure 3 - Reflectance curves of a preliminary
dyeing of the OG 107 shade on nylon,
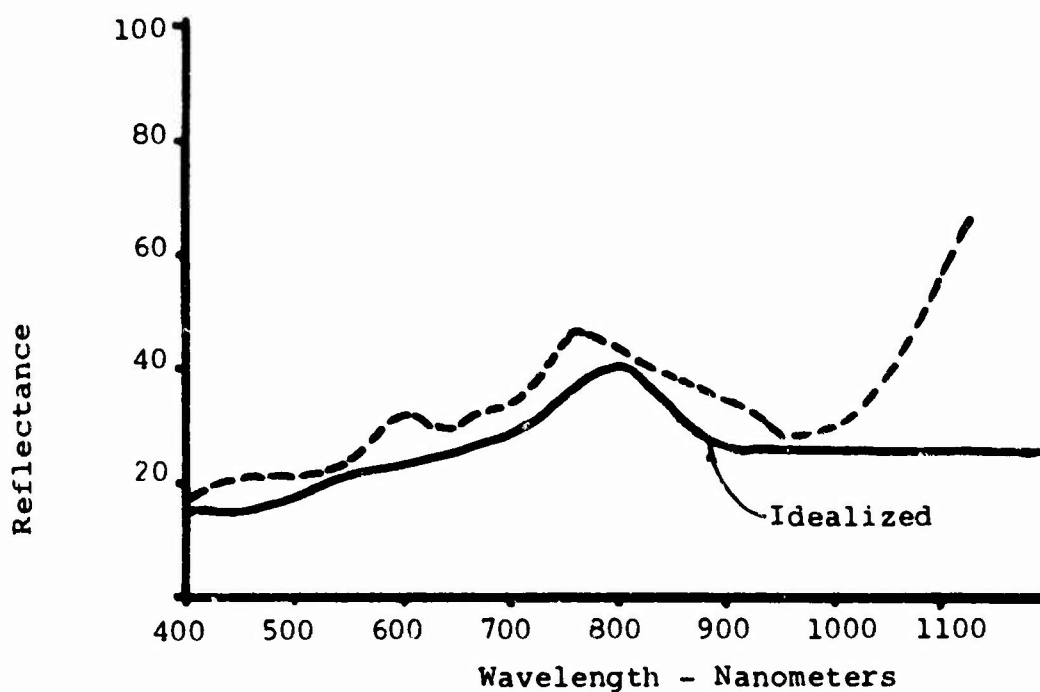and the idealized OG 107 shade

Figure 4 - Reflectance curves of a preliminary dyeing
of the Tan 337 shade on nylon, and the
idealized Tan 337 shade

Table V

Shade and Strength of Color Matches

	x	y	Color Strength
OG 107	.348	.375	reference
OG 107 "with IR"	.352	.366	55%
Tan 337	.344	.347	reference
Tan 337 "with IR"	.351	.340	77%

No further color matching work was done, as it was deemed unwarranted due to the poor light stability of IR 99.

D. Results

1. Infrared absorber 99 will dye onto nylon 6,6 in heavier shades if the nylon fabric has been previously dyed with an acid dye. At 0.2% level, at least 85% of IR 99 transferred from the dye bath to the fabric with 1% acid dye.

2. When IR 99 is after-dyed on nylon already dyed with Acid Blue 113 (a bis-azo dye, see structure No. 9, Appendix II), the absorption band at 960 nm is intensified.

3. Pretreating nylon with various organic salts, at a low level (0.5% o.w.f.) increased the dyeability of IR 99 at pH 6.5 by about 50% but higher levels of salts gave divergent results.

4. A large amount of the sodium salt of saccharin in the dyebath, 20% on weight of fiber, greatly increased the exhaust of IR 99 from the dye bath.

5. A large amount of potassium acid phthalate at pH 5 in the dyebath of IR 99, prevented the dyeing of IR 99.

6. Infrared absorber 117, did not exhaust well in any of its dyeings.

7. IR 99 dyed on previously acid dyed nylon was less light-stable than IR 99 dyeings without the colorants.

8. IR 99 dyed in the presence of a high concentration of the sodium salt of saccharin had reduced light-stability.

9. In a Fadeometer, the infrared absorber IR 99 is slightly faded by infrared light, more by visible and mostly by ultraviolet light.

E. Discussion of Results

The concept of placing acid dyes on nylon to provide anionic sites proved well founded as consistly good dyeings of IR 99 were obtained with predyed samples as is shown by samples 14 through 29 in Table I. From analyses of the exhausted dyebaths (Table III) 85 to 97 percent of the infrared absorber went onto the cloth predyed with acid dyes. This data was used to determine the amount of the infrared absorber on the cloth. From the net concentration of IR 99 and the infrared reflectances, the absorbency index a_r, (Appendix I) was calculated to be near 6.0 (Table III). However, the IR 99 dyeings on the Acid Blue 113 samples absorbed much more strongly at 960 nm than on the other dyed fabrics. The absorbency index, a_r, if IR 99 on cloth dyed with Acid Blue 113 is 12.9 compared to the average value of 6.0 found on other dyed fabrics. This appears to be due to an interaction between IR 99 and Acid Blue 113 to yield a new compound or a complex having increased infrared absorption.

The unbuffered dyeings of IR 99 on nylon at pH's 3, 5, 7 and 9 removed only 30% of the dye from the dye bath and thus put approximately 0.06% by weight of IR absorber on each fabric sample. Adding salts at 0.5% on the weight of the fiber (samples 8-12) increased the dye exhaust to 50%. Larger amounts of citrate and phthalate decreased the uptake of dye, but a larger concentration of the sodium salt of saccharin at its natural pH of 5.4 effected a substantially complete exhaust of IR 99. The absence of dyeing in the 20% on the weight of the fiber of phthalate and the complete dyeing in 20% on the weight of the fiber of the saccharin salt (Table I, samples 6 and 7) is certainly striking. Hacklander et. al. (7) in their patent stated qualitatively that salts of saccharin added to dyebaths allowed greater shade build-up at a lower dyeing temperature (165°F).

All the dyeings of IR 117 were weak even when made on nylon predyed with acid dyes. Since the acid dyes provided sites for IR 99, then it appears that the IR 117 was not diffusing to the sites. The IR 117 is a much larger molecule than IR 99 and its cationic charge is probably made more diffuse by being spread over this larger molecule, and thus the attractive forces between dye and substrate are weaker.

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The light stability tests were done in a Fadeometer, which does not exactly match the sun's spectrum as a light source. The carbon arc is much stronger than sunlight from 340 to 420 nm and much weaker in the visible region, but approximately equal to sunlight in the infrared region. The tests behind an ultraviolet screen and a red filter indicated that about 10 percent of the fading of IR 99 was caused by the infrared radiation, about 30 to 40 percent by visible light and the rest by the ultraviolet light (Table IV).

Although the acid dyes on the fabric improved the dyeability of IR 99, they did not improve its light stability. The Acid Blue 113 - IR 99 interaction had about the same light stability as IR 99 dyed with the other acid dyes. The sodium saccharin assisted dyeing did not improve the lightfastness, as might be expected from Hacklander et. al. (7) who found an increase in lightfastness of basic dyes dyed in the presence of saccharin. The polybasic acid salts such as sodium citrate have been described as preventing discoloration and fading of fluorescent whitening agents by Yoshikawa et.al. (8), but overall give no drastic improvement to the light stability of IR 99. Also, the ultraviolet absorber, UV 284, overall did not raise the lightfastness ratings of IR 99, principally because so much fading was caused by visible and infrared light. In general, the better lightfastnesses were associated with the poorer dyeings. Since the dyes did not improve the lightfastness of the IR 99 as might be expected through a filter action, then it may be that energy is transfered from the dyes to the IR 99, thus increasing the rate of photodegradation of IR 99. It should be noted that higher amounts of these infrared absorbers along with ultraviolet absorbers in plastics are known to perform well in light stability tests, for example, windows in plastic welding goggles withstand many hours of welding radiation.

The reflectance curves of the OG 107 and Tan 337 preliminary dyeings have the same general shape of the ideal OG 107 and Tan 337 curves even though considerably weaker to the eye.

Also, the IR 99 is weaker on the tan shade than on the OG 107 sample. This may be due to the smaller amount of acid dyes on the tan nylon than on the OG 107 nylon.

F. Conclusions and Recommendations

In order to obtain at least a 0.2% dyeing of IR 99 onto nylon, some assistance is needed, such as previously applying an acid dye or using a high concentration of sodium salt of saccharin in the dyebath.

However, the light stabilities of the best dyeings of IR 99 are poor being less than 5 hours in a Fadeometer. The fading caused by visible and near infrared radiation is substantial and is not retarded by the screening action of dyes.

A practical absorptive camouflage will require a much more light stable infrared absorber than IR 99, but there is presently no obvious method of increasing its stability by structural changes.

The best recommendation at this time for developing a formulation of dyes that approach the ideal camouflage curve is to search for acid dyes with strong infrared absorption bands. The spectra of metallized dyes containing Cr^{+3}, Mn^{+2}, Ni^{+2}, Co^{+2}, Cu^{+2}, Fe^{+2} and Fe^{+3} in particular should be examined. The dyes should be inherently more light stable than the present aminium-cation compounds.

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Appendix I

Calculations:

The changes in strength of the infrared absorbers due to fading were calculated by the Kubelka-Munk relationship of the reflectance values of the infrared absorption maxima (Ref. 2).

$$\text{fraction remaining} = \frac{C_x}{C_o} = \frac{(Fr)\,tx - (Fr)\,u}{(Fr)\,to - (Fr)\,u}$$

where C_x = concentration of IR absorber in fabric after exposure in Fadeometer

C_o = concentration of IR absorber in fabric before exposure in Fadeometer

$$(Fr)\,tx = \frac{(1-R_x)^2}{2\,R_x}$$

$$(Fr)\,to = \frac{(1-R_o)^2}{2\,R_o}$$

$$(Fr)\,u = \frac{(1-R_u)^2}{2\,R_u}$$

where R_x = reflectance at 960 nm of the fabric dyed with IR absorber after exposure in Fadeometer

R_o = reflectance before exposure in Fadeometer

R_u = reflectance of fabric with no IR absorber

The Fr values for reflectance (R) values (sometimes called K/S values) can be read from the fifth column in the table in Appendix C of reference 2.

At 900 to 960 nanometers, all the dyes and organic acid agents, except Acid Blue 158, had no absorption. Therefore, for the reflectance Ru of untreated nylon, 87.5 per cent was used.

Since Acid Blue 158 has an absorption band at 960 nm, the reflectance Ru for the 1.0% dyeing of Acid Blue 158 is 47 per cent.

The dyeing absorbency index, Ar, can be calculated from the formula:
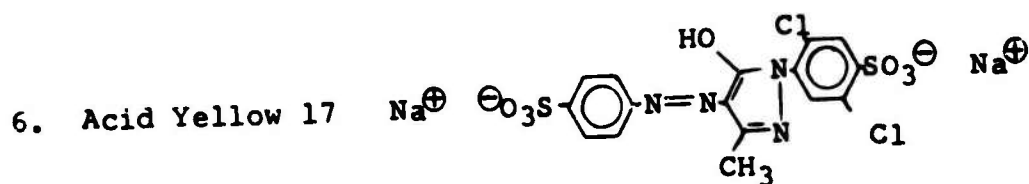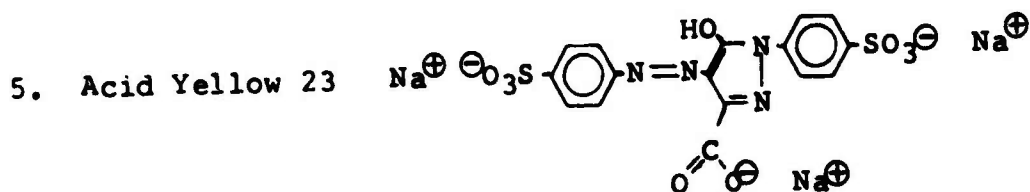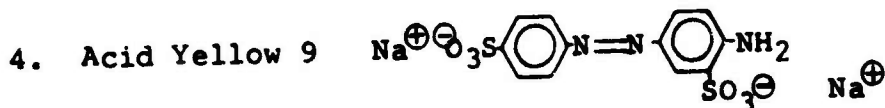
$$Ar = \frac{(Fr)\,to - (Fr)\,u}{C_o}$$

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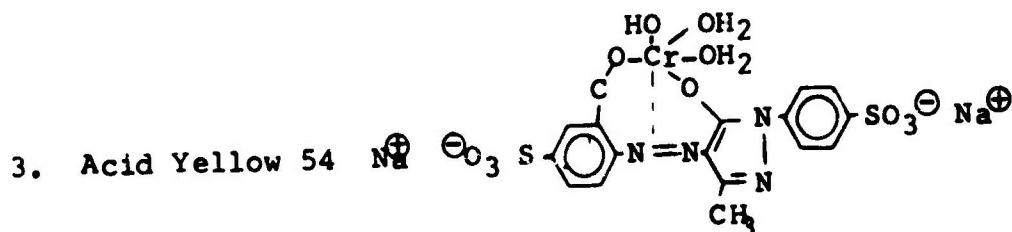## Structures of Compounds

1. Cyasorb IR 99
   Light Absorber
   m.w. 694.93

$$\left((C_2H_5)_2 \; N \!-\!\! \bigcirc \right)_3 \; N^{\oplus} \quad SbF_6^{\ominus}$$

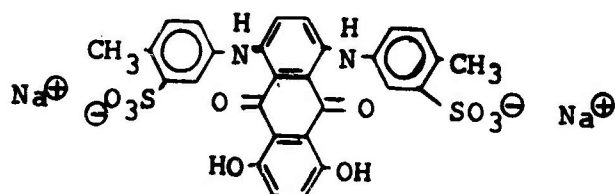2. Cyasorb IR 117
   Light Absorber
   m.w. 932.70

$$\left((C_2H_5)_2 \; N \!-\!\! \bigcirc \right)_2 \; \overset{\oplus}{N} \!-\!\! \bigcirc \!-\! N \left(\bigcirc \!-\! N(C_2H_5)_2 \right)_2$$

$$SbF_6^{\ominus}$$

3. Acid Yellow 54

$$Na^{\oplus} \quad {}^{\ominus}O_3S \!-\!\! \bigcirc \!-\! N\!=\!N \quad \overset{HO \;\; OH_2}{\underset{O}{\overset{|}{\underset{}{Cr}}}\!-\!OH_2} \quad N \!-\!\! \bigcirc \!-\! SO_3^{\ominus} \; Na^{\oplus}$$

CH₃

4. Acid Yellow 9

$$Na^{\oplus} \, {}^{\ominus}O_3S \!-\!\! \bigcirc \!-\! N\!=\!N \!-\!\! \bigcirc \!-\! NH_2$$

$$SO_3^{\ominus} \quad Na^{\oplus}$$

5. Acid Yellow 23

$$Na^{\oplus} \; {}^{\ominus}O_3S \!-\!\! \bigcirc \!-\! N\!=\!N \quad \overset{HO}{\underset{N}{\bigcirc}} \!-\!\! \bigcirc \!-\! SO_3^{\ominus} \; Na^{\oplus}$$

$$O\!=\!C\!-\!O^{\ominus} \quad Na^{\oplus}$$

6. Acid Yellow 17

$$Na^{\oplus} \; {}^{\ominus}O_3S \!-\!\! \bigcirc \!-\! N\!=\!N \quad \overset{HO \;\; Cl}{\underset{CH_3}{\bigcirc}} \!-\!\! \bigcirc \!-\! SO_3^{\ominus} \; Na^{\oplus}$$
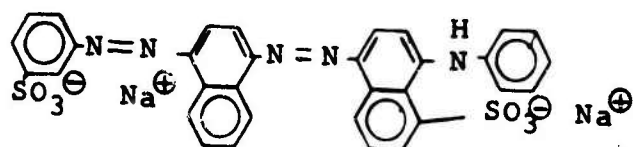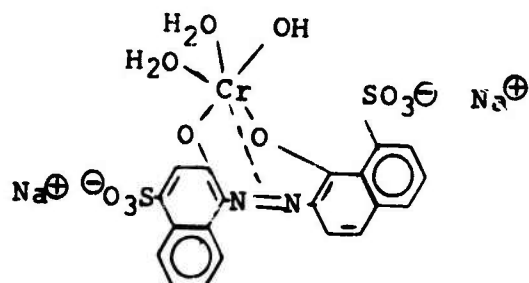
Cl
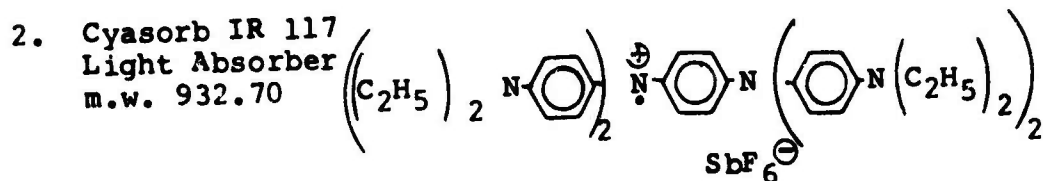
7. Acid Yellow 34
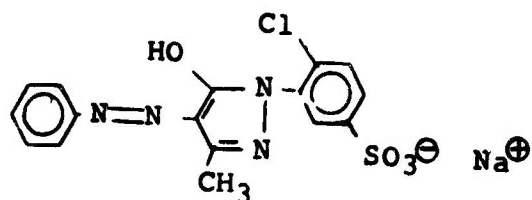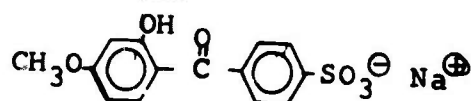

8. Acid Green 41

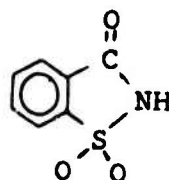9. Acid Blue 113

10. Acid Blue 158

11. Cyasorb UV 284
Light Absorber
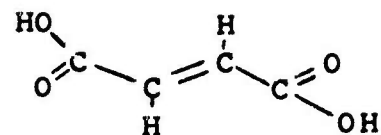$pK_a \sim 2$

Sodium 4'-methoxy-2'-hydroxybenzophenone-
4-sulfonate
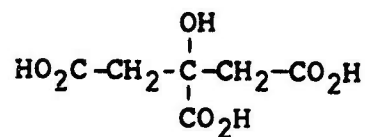
12. Saccharin
$pK \sim 2.5$

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13. Fumaric Acid
    pK 3.0, 4.5

$$HO_2C-CH=CH-CO_2H$$

14. Citric Acid
    pK 3.1, 4.7, 5.4

$$HO_2C-CH_2-\underset{\underset{CO_2H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CO_2H$$

15. Phthalic Acid
    pK 2.9, 5.5

$$C_6H_4(CO_2H)_2$$
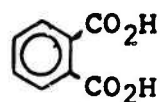
APPENDIX III

Methods of Application

1. **Acid Dyes**

    10 gm nylon 6,6 fabric
    5 ml 10% ammonium chloride solution
    Dye(s) distilled water to 400 ml total bath volumes.
    Wetted out fabrics are entered into dye baths, worked
    5 minutes at 120°F, temperature raised to boil over
    30 minutes. Dyeing is run 60 minutes at the boil.
    After reaching the boil, 1% acetic acid (28%) (o.w.f.)
    is added to dveings to improve exhaustion.

2. **Metallized acid dyes**

    10 gm nylon 6,6 fabric
    4 ml 5% formic acid (2% o.w.f.)
    Dye(s) distilled water to 400 ml total bath volume.
    Wet out fabrics are entered into dye baths and worked
    5 minutes at 60°F. Temperature is raised to the boil,
    dyeings are run for 1 hour at the boil.

    After dyeing, all fabrics are rinsed thoroughly in
running tap water, then ironed dry at wash-and-wear setting.

3. **Pretreating nylon with organic salts.**

    Bath with 0.5% or 5.0% (o.w.f.) of organic salt
    (sodium salt of saccharin, potassium citrate, pot-
    assium acid phthalate, sodium fumarate, UV 284 ultra-
    violet absorber) is adjusted to pH 3.5. Nylon cloth
    is entered, bath is heated to boil for 1 hour.

    Infrared absorber after-treatment is made from the
    same bath, by raising pH to 6.5 and adding aliquot of
    IR absorber.

4. **Dyeing Infrared Absorbers on Nylon 6,6.**

    a. Infrared stock solutions

        (1)   50 mg IR Absorber IR 99
              50 mg Sulfamic Acid
              0.5 ml 5% Deceresol NI (a polyether alcohol
    surfactant). Paste together, heat with 25 ml water to
    boil to obtain a clear solution. Dilute to 200 ml with
    water. Aliquot 80 ml/20 mg IR Absorber.

(2)   50 mg IR Absorber IR 99
      5 ml Acetone
      0.5 ml 5% Deceresol NI

    Dissolve components together, dilute to 200 ml with water. Aliquot 80 ml/20 mg IR Absorber.

(3)   200 mg IR 99 dissolved 50
      50 ml Acetone
      0.5 ml 5% Deceresol NI

    Dilute to 100 ml with water. Aliquot 10 ml/20 mg IR Absorber.

NOTE: This formula probably best method for scale up dyeing.

(4)   100 mg IR-117 dissolved in 125 ml acetone
      125 ml acetone

    Dilute to 200 ml with water. Aliquot 40 ml/20 mg IR Absorber.

b.   Dyeing Procedure

    For dyeing 0.2% (o.w.f.) of infrared absorber 20 mg per 10 gms of nylon cloth is required. Therefore, the aliquot of stock solution is diluted to 400 ml with water, the pH is adjusted to proper pH, usually 6.5 to 7.0 and the dyeing is run for one hour at the boil, then rinsed out and dried.

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