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ABSORBERS OF NEAR INFRARED RADIATION

by

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FOREWORD

The control of the IR absorption characteristics of textile surfaces, and of many other media, is particularly significant in the area of camouflage but has many other potential applications in both military and civilian areas. There are several ways to achieve this control, but the ideal is the colorless compound which is effective without introducing secondary problems requiring solution.

The major significance of the products studied as part of the work being reported is not the degree of their effectiveness but rather the underlying demonstration that the interrelationship of chemical structure and resonance phenomena, so well established in the visible, can be extended into the longer wavelength bands. With this demonstration improved products may be expected to arise as research efforts continue.

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ABSTRACT

Four methods have been available to bring infrared reflectance to values that afford optimum camouflage against detection by devices such as the sniperscope. One difficulty with these has been their limitation to dark combat shades. No useful method has been found to produce light shades such as Khaki 1, with low values of IR reflectance in the 1-micron region of the spectrum.

This report describes results with two new compounds that have recently become available on a limited commercial basis. Results are based on the ability of these compounds to absorb more strongly the radiation in the region from 0.9 to 1.1 microns than that in the visible region of the spectrum.

ABSORBERS OF NEAR INFRARED RADIATION

I. Introduction

One of the requirements for good camouflage against detection by active infrared devices such as the sniperscope is that the reflectance in the spectral region between 0.9 and 1.1 microns be controlled. As the result of several field studies, the Corps of Engineers has recommended a reflectance of about 20 percent relative to magnesium oxide as optimum.⁽¹⁾ This value, applied to all terrains including sandy deserts and snow cover, is substantially lower than that afforded by commonly used dyestuffs.

Four methods have been found to lower infrared reflectance to acceptable levels:⁽²⁾

a. Sulfur dyes - Most sulfur dyes absorb strongly in the near-infrared as well as in the visible region of the spectrum. When applied alone, or when a vat-dyed ground shade is topped with sulfur dyes, or when sulfur dyes and vat dyes are applied together, acceptable levels of reflectance can be attained. However, the poor colorfastness characteristics of these systems preclude their use for military purposes.

b. Resin-bonded pigments - Certain pigment colorants, notably inorganic pigments and carbon black, can lower infrared reflectance to suitable levels, but some type of resin binder is required to fix these to a fabric. A broad study of this problem conducted in 1953^(2,3) on fabrics commercially prepared in this manner showed that all fastness characteristics were good except to laundering, either with or without a chlorine bleach. However, since 1953, many new resin binders have been developed which add substantially to the washfastness of resin-bonded pigment systems.

c. Special vat dyes - A series of vat dyes were developed under contract^(3,4) that made it possible to achieve an infrared reflectance of 20 percent in an Olive Green 107 shade. The formulation using these special vat dyes showed colorfastness at least as good as the standard formulation in all respects except to high concentrations of chlorine-emitting compounds that are used for CW protection. Since these developments, another vat dye (Cibanone Gray 2GR) has been produced by which it is possible to produce olive green shades with sufficiently low infrared reflectance, but this dye also is somewhat unstable to chlorine-emitting compounds in high concentrations.

D. Cuprous sulfide treatment - Sheldon, et al., reported in 1953 that a treatment involving cuprous sulfide could lower infrared reflectance⁽⁵⁾ but the treatment was somewhat involved and difficult to control. Furthermore, the result did not have sufficient durability to be implemented.

As pointed out above, ideal infrared camouflage requires low reflectance in the 1 micron region, even for uniforms intended for use in desert and snow-covered terrains.⁽¹⁾ It has long been hoped that some substance would be discovered that has weak absorption in the visible portion of the spectrum and strong absorption in the near infrared. This goal has been communicated to the domestic dyestuff industry.

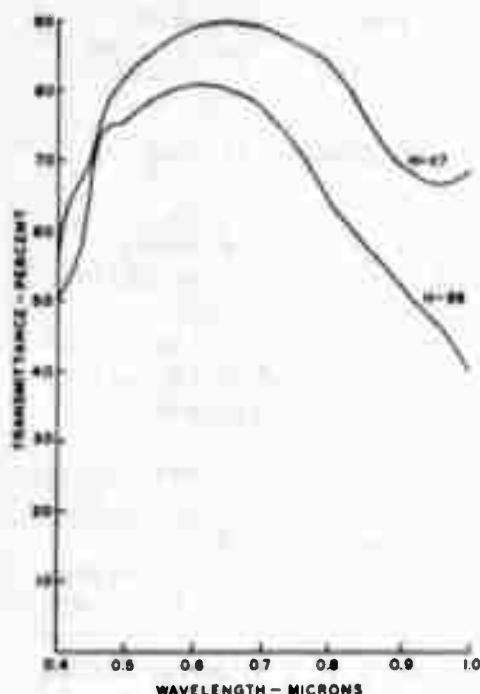


Figure 1: Transmittance of films of B-15 binder on glass microscope slides.

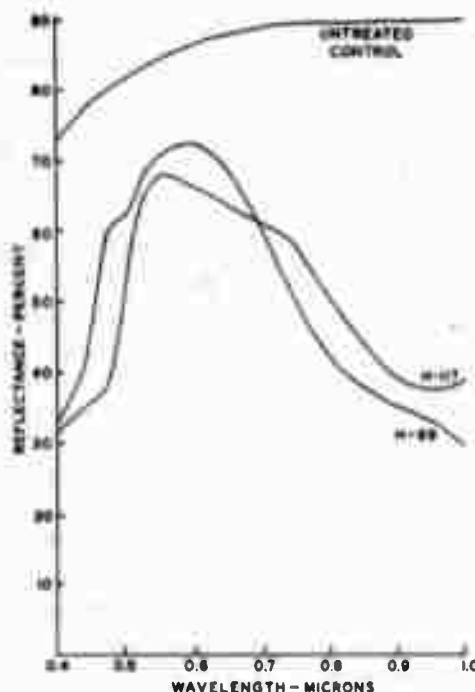


Figure 2: Reflectance of Cloth, Cotton, Sateen, 9 oz./yard, undyed, treated with two infrared absorbers, and of an untreated control.

Recently, the American Cyanamid Company released experimental quantities of two organic compounds (H-99 and H-117) that absorb rather strongly in the near infrared. These compounds, pale yellow-green in color, were developed primarily for use in sun glasses. Figure 1 shows the transmittance of films of these compounds from 0.4 to 1.0 micron. Figure 2 shows the reflectance curves of the compounds applied to undyed cotton sateen over the same spectral range. These curves, demonstrate the possibility of achieving low infrared reflectance

with a near colorless substance. This report discusses the results of an evaluation of these two compounds from the standpoint of durability. Both compounds were applied to all-cotton and nylon/cotton (Nycot) sateens both undyed and dyed to OG-107. The fabrics were subjected to color-fastness tests with respect to wet cleaning, laundering, light, and weathering.

II. Experimental Procedures

A. Sample Preparation

Two type of fabrics were involved in the tests:

A 9-oz cotton sateen, undyed but prepared for dyeing (desized, boiled off, scoured, and bleached); and the same fabric dyed OG-107 with the following vat dyes -

Vat Black #25 C.I. 69525
Vat Green #8 C.I. 71050
Vat Green #3 C.I. 69500
Vat Yellow #2 C.I. 67300

An 8.5-pz cotton/nylon (Nycot) sateen, undyed but prepared for dyeing; and the same fabric with the cotton portion dyed as above but with the nylon portion dyed with the following premetallized dyes -

Neutral Premetallized Green 2BL
Neutral Premetallized Yellow 2RL
Acid Orange #86
Neutral Premetallized Blue G

The four fabric samples were cut into strips. One strip was joined to one of each of the other three fabrics by sewing them end to end. Each set of four fabrics was treated with one of the following eight finishes:

Finish I - IR Absorber H-99 (0.1%) plus 5% Rhoplex B-15.

Finish II - IR Absorber H-117 (0.03%) plus 5% Rhoplex B-15.

Finish III - IR Absorber H-99 (0.1%) plus Cyasorb UV-24 (0.2%) plus 5% Rhoplex B-15.

Finish IV - IR Absorber H-117 (0.03%) plus Cyasorb UV-24 (0.2%) plus 5% Rhoplex B-15.

Finish V - Cyasorb UV-24 (0.2%) and 5% Rhoplex B-15.

Finish VI - IR Absorber H-99 (0.1%).

Finish VII - IR Absorber H-117 (0.3%)

Finish VIII - Cyasorb UV-24 (0.2%)

Acetone was selected as the solvent for each formulation because it dissolved the IR absorbers, the B-15, and the UV absorber. All the ingredients were compatible.

The fabrics were padded on a 3-roll padder, squeezed, and dried at 250°F for 5 minutes. Wet pickup was 80%.

Samples of the identical Nyco fabrics used for the above applications were also submitted to American Cyanamid to enable them to apply their compounds in their own way. American Cyanamid chose to apply only the IR Absorber H-117. They did not specify the binder and ultraviolet absorbers used.

B. Test of Colorfastness and Durability of IR Reflectance

Samples 2" x 4" for wet cleaning and laundering and 2½" x 8" for fading and weathering were swatched from each of the treated strips and, together with a set of controls, were subjected to the colorfastness tests shown in table I.

TABLE I

DURABILITY TESTS PERFORMED

<u>Colorfastness to:</u>	<u>Method No.</u>	<u>Remarks</u>
Wet cleaning	5622*	Liquid used was Stoddard Solvent
Laundering	IV-A**	
Light	5660*	Dyed samples - 100 hours Undyed samples - 20 hours
Weathering	5671*	With water spray for 64 hours in Atlas Weatherometer

*Federal Specification Textile Test Methods, CCC-T-191b.

**AATCC Laundering Method

C. Reflectance and Colorimetric Measurements

Reflectance measurements were made on all the samples using the Quartermaster Infrared Photometer. This device has the same spectral sensitivity as the sniperscope.

Spectral reflectance curves were obtained using the General Electric Recording Spectrophotometer in the region of from 0.4 to 1.0 micron. These curves were integrated in the visible region of the spectrum, with respect to the Standard Observer and Source "C", by using the Librascope Tristimulus Integrator.

III. Results and Discussion

A. Effect of Treatments on Reflectance and Color

Table II shows the infrared reflectance values, relative to the sensitivity functions of the sniperscope, of the four fabrics before and after the various treatments. It can be seen that both of the infrared absorber compounds under review reduced the infrared reflectance substantially. The ultraviolet absorber (Cyasorb UV-24) appears to have had a small but significant influence of its own.

TABLE II

INFRARED REFLECTANCE OF FABRICS BEFORE AND AFTER
TREATMENT WITH INFRARED
AND ULTRAVIOLET ABSORBERS

	Untreated	Treated								
	<u>Orig</u>	<u>I</u>	<u>II</u>	<u>I&II</u>	<u>II&III</u>	<u>III</u>	<u>IV</u>	<u>V</u>	<u>VI</u>	<u>C</u>
Dyed Cotton	41	21	33	17	28	37	19	23	38	--
Undyed Cotton	80	30	50	24	45	64	25	40	58	--
Dyed Nyco	42	23	32	17	29	39	18	27	36	--
Undyed Nyco	72	27	53	18	34	66	25	47	60	30

Note Finish I - Infrared Absorber H-99 with B-15 binder.
 II - Infrared Absorber H-117 with B-15 binder.
 III - Ultraviolet Absorber Cyasorb UV-24 with B-15 binder.
 IV - Infrared Absorber H-99 applied from solvent alone.
 V - Infrared Absorber H-117 applied from solvent alone.
 VI - Ultraviolet Absorber Cyasorb UV-24 applied from solvent alone.
 C - Application by American Cyanamid.

Table III summarizes the colorimetric data to show the influence of these treatments on the visual appearance of the dyed cotton and Nyco. These data show that the absorbers had little influence on color in shades as deep as Olive Green 107.

TABLE III
COLORIMETRIC DATA ON FABRICS TREATED WITH
INFRARED AND ULTRAVIOLET ABSORBERS

<u>Sample</u>	<u>Lightness</u> <u>Δ Y (%)</u>	<u>Chromaticity</u> <u>Δ C MacAdam</u>	<u>Total Color</u> <u>Δ E MacAdam</u>
<u>Dyed Cotton</u>			
H-99 with B-15	-0.06	0.5	0.5
H-117 with B-15	-0.36	0.8	1.5
H-99 and UV-24 with B-15	-0.17	0.3	0.5
H-117 and UV-24 with B-15	0.73	1.5	3.0
UV-24 with B-15	0.44	2.8	3.0
H-99 (Solvent)	0.09	1.3	1.5
H-117 (Solvent)	-0.10	0.6	0.5
UV-24 (Solvent)	0.31	0.2	1.0
<u>Dyed Nyc</u>			
H-99 with B-15	0.65	0.7	2.5
H-117 with B-15	0.26	0.8	1.5
H-99, UV-24, B-15	-0.49	0.7	2.0
H-117, UV-24, B-15	0.50	1.2	2.0
UV-24 with B-15	0.30	0.8	1.5
H-99 (Solvent)	-0.03	0.6	0.5
H-117 (Solvent)	0.81	1.0	3.0
UV-24 (Solvent)	-0.39	0.4	1.5
H-117 (M. Cy.)	0.14	0.6	0.9

The data in Tables II and III together show that reflectance can indeed be controlled in the infrared without significant effect on visual shade. Figure 3 shows the influence of the infrared absorbers on the reflectance curves of the nylon/cotton sateen dyed OG-107.

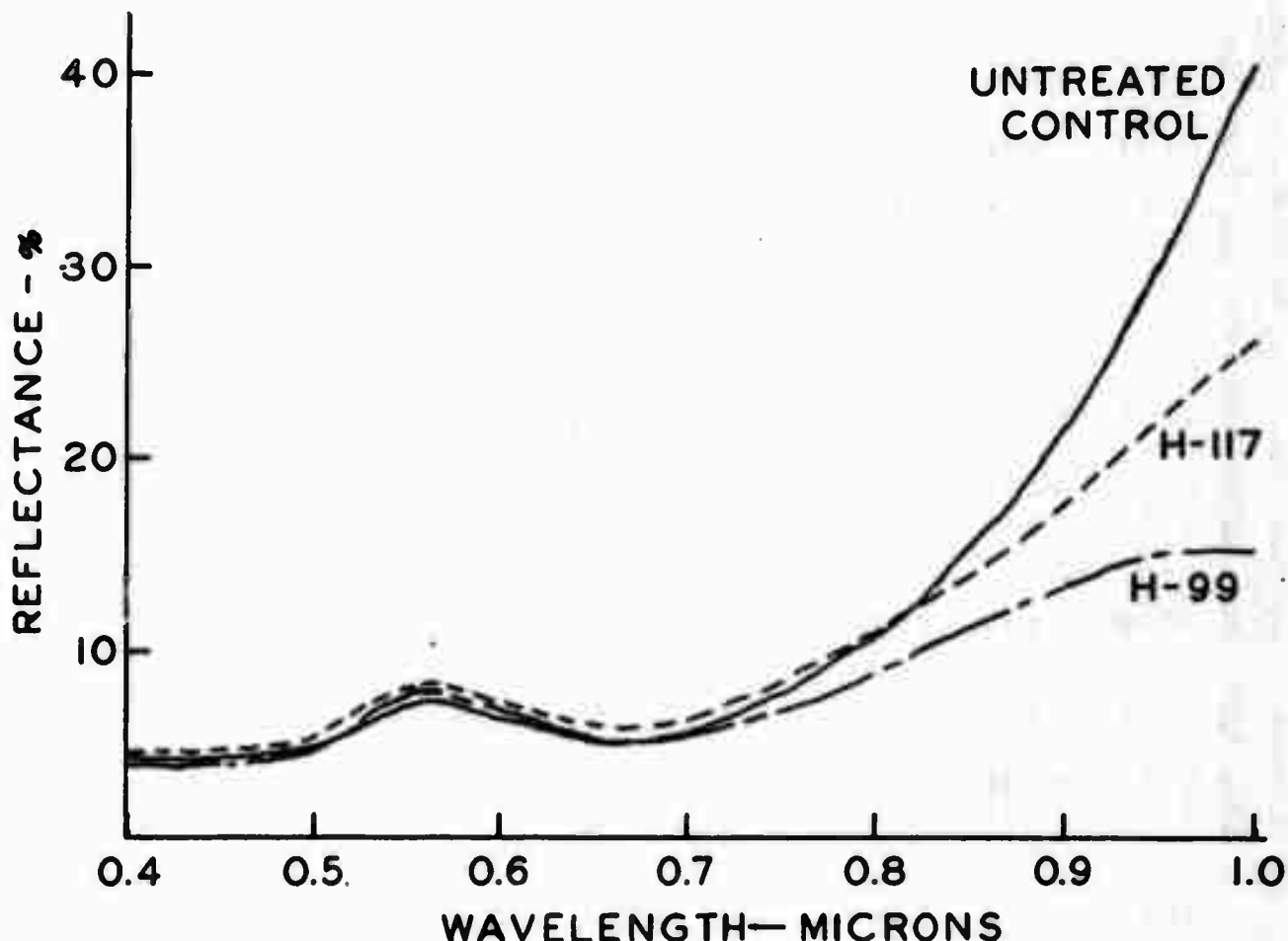


Figure 3: Reflectance of Cloth, Nylon/Cotton, 8.5 oz/yd², Olive Green 107, treated with two infrared absorbers, compared with untreated control.

B. Durability of IR Reflectance and Color

To be practical, a military fabric must be durable to the stresses encountered in actual use. The colorfastness tests, the results of which are discussed below, attempt to simulate these stresses. Reflectance, as obtained with the Quartermaster Infrared Photometer, is given in the first columns of Table IV. The columns headed by $\Delta (K/S)$ show the changes in quantity of absorbing matter as a result of the colorfastness tests. The negative sign indicates a loss of colorant. The data for these columns were obtained at 1.0 micron with the General

TABLE IV. COLOR AND REFLECTANCE OF FOUR FABRICS AND NINE FINISHES BEFORE AND AFTER DURABILITY TESTS

Finish	Fabric	Control	After Wash Cleaning			After Laundering			After Fastness			After Weathering		
			Reflectance	$\Delta(E/s)$	\$ Lost	Reflectance	$\Delta(E/s)$	\$ Lost	Reflectance	$\Delta(E/s)$	\$ Lost	Reflectance	$\Delta(E/s)$	\$ Lost
None	Dyed Cotton	41	43	-0.03	10	43	-0.03	10	40	+0.03	3	47	-0.05	17
	Undyed Cotton	80	77		..	76		..	77		..	81		..
	Dyed Nyco	42	42	-0.03	10	43	-0.03	10	42	-0.03	10	45	-0.04	14
	Undyed Nyco	72	71		..	71		..	72		..	74		..
H-99 with B-15	Dyed Cotton	21	36	-1.04	71	34	-0.86	58	37	-0.52	35	44	-1.17	80
	Undyed Cotton	30	48	-0.63	71	51	-0.71	80	58	-0.80	90	78	-0.88	100
	Dyed Nyco	23	30	-0.22	26	30	-0.04	5	38	-0.32	38	31	-0.51	60
	Undyed Nyco	27	51	-0.92	90	52	-0.90	88	52	-0.79	78	73	-1.01	100
H-117 with B-15	Dyed Cotton	33	40	-0.19	37	36	-0.09	18	39	-0.19	37	46	-0.23	45
	Undyed Cotton	50	60	-0.02	50	51	+0.06	+100	74	-0.08	96	79	-0.06	100
	Dyed Nyco	32	40	-0.33	47	32	-0.17	24	40	-0.25	36	41	-0.37	53
	Undyed Nyco	53	68	-0.02	65	53	-0.02	+60	71	-0.03	90	73	-0.03	100
H-99 and UV-24 with B-15	Dyed Cotton	17	33	-1.62	78	33	-1.46	70	37	-1.62	78	42	-1.67	80
	Undyed Cotton	24	45	-1.66	95	47	-1.60	91	37	-1.50	86	75	-1.75	100
	Dyed Nyco	17	32	-1.14	78	28	-1.06	64	36	-2.33	86	37	-2.35	86
	Undyed Nyco	18	42	-2.30	91	47	-2.30	91	43	-1.28	51	72	-2.52	100
H-117 and UV-24 with B-15	Dyed Cotton	28	40	-0.14	26	30	0.00		38	-0.14	26	45	-0.23	43
	Undyed Cotton	45	66	-0.04	29	52	-0.03	22	66	-0.07	51	77	-0.13	100
	Dyed Nyco	29	41	-0.13	25	33	-0.07	13	38	-0.13	23	41	-0.20	36
	Undyed Nyco	34	64	-0.22	90	57	-0.12	49	68	-0.16	65	72	-0.25	100
UV-24 with B-15	Dyed Cotton	37	40	-0.10	22	41	-0.10	22	40	-0.12	27	45	-0.14	32
	Undyed Cotton	64	75	-0.02	..	75	-0.02	..	78	-0.02	..	79	-0.02	..
	Dyed Nyco	39	41	-0.01	3	43	+0.01	+3	43	-0.03	10	44	-0.05	15
	Undyed Nyco	66	70	0.00	..	70	0.00	..	71	0.00	..	73	0.00	..
H-99	Dyed Cotton	19	36	-1.23	74	27	-0.62	37	33	-1.11	66	45	-1.36	81
	Undyed Cotton	25	49	-0.67	82	50	-0.75	92	49	-0.15	60	80	-0.82	100
	Dyed Nyco	18	32	-1.08	55	30	-1.12	57	31	-1.22	62	32	-1.34	68
	Undyed Nyco	25	50	-0.73	86	47	-0.65	77	42	-0.18	21	73	-0.84	100
H-117	Dyed Cotton	28	40	-0.12	27	38	-0.08	18	37	-0.07	16	45	-0.17	38
	Undyed Cotton	40	63	-0.23	92	54	-0.17	68	72	-0.24	95	79	-0.25	100
	Dyed Nyco	27	39	-0.54	63	31	-0.40	47	36	-0.50	58	39	-0.56	65
	Undyed Nyco	47	67	-0.12	92	60	-0.08	62	51	-0.02	18	71	-0.13	100
UV-24	Dyed Cotton	38	41	-0.02	5	39	-0.01	3	40	-0.09	23	46	-0.10	26
	Undyed Cotton	58	71	-0.03	26	68	-0.02	5	76	-0.03		80	-0.03	
	Dyed Nyco	36	41	-0.11	26	39	-0.11	26	40	-0.15		43	-0.15	36
	Undyed Nyco	60	70	-0.02		65	-0.02		71	-0.02		73	-0.02	
H-117 (Am. Cy)	Dyed Nyco	20	22	-0.19	14	26	-0.11	7	35	-0.77	55			
	Undyed Nyco	30	32	-0.08	11	40	-0.02	3	49	-0.49	68			

Electric Recording Spectrophotometer. The next columns show the percentage of colorant that has been lost. The double asterisk (**) means that no material absorbing at one micron was present on the control and hence no change was observed.

1. Fastness to Wet Cleaning

It can be seen from Table IV that wet cleaning had little influence on the infrared reflectance of the untreated controls. Some loss of infrared reflectance may be noted, however, for the treated samples. Comparing the American Cyanamid sample with our samples treated with IR absorber H-117 and B-15 suggests that the selection of the binder is the most critical factor with respect to color fastness to wet cleaning.

2. Fastness to Laundering

The loss in control of infrared reflectance due to laundering was comparable to that due to wet cleaning. For a few of the undyed samples, an increase in $\Delta K/S$ was observed, probably due to a slight accumulation of soil or other absorbing substance during laundering.

3. Fastness to Light

Since the undyed samples were exposed for only 20 hours in the Fadeometer, it is obvious from the data that the infrared absorbers were very fugitive. The ultraviolet absorber had a slight but hardly significant influence on the degree of fading.

4. Fastness to Weathering

Table IV shows that, after exposure in the Weatherometer, control of infrared reflectance by the infrared absorbers was completely lost. This is not surprising in view of the lack of fastness to light demonstrated above.

IV. Conclusions

It has long been the opinion that it is not possible to produce organic colorants with electronic absorption bands located primarily in the infrared. These samples are the first organic compounds we have seen that have demonstrated strong absorption near 1 micron and yet little absorption in the visible region of the spectrum. Thus, for the first time, it becomes possible with organic substances to lower the infrared reflectance of shades as light as Khaki 1 to acceptable levels.

The results of the durability evaluations of these compounds suggest that any optimism must be tempered by the realization that substantial improvement in resistance to photo-degradation is required before these materials can be used as textile colorants.

V. Acknowledgements

We wish to acknowledge the assistance of Mrs. Ruth J. Evans of this Branch, who performed the colorfastness tests, and of Mr. Alfred Merola, who assisted in the colorimetric measurements. Dr. Ralph Coleman, American Cyanamid Company, provided confirmatory data. Dr. R. B. Van Order of American Cyanamid Company made the product samples available for our study.

We wish to acknowledge the effort that American Cyanamid Company has placed in this area as a continuing phase of efforts originally stimulated by a research program on IR colorants for the Department of the Army, undertaken during the early 1950 period.

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