AD A110824

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

REPORT NUMBER: 14076.2-C; 17451.1-C

2. GOVT ACCESSION NO: AD-A110 824

3. RECIPIENT'S CATALOG NUMBER:

TITLE (and Subtitle): Modeling the Infrared Reflectance and Emittance of Paints and Coatings

5. TYPE OF REPORT & PERIOD COVERED: Final: 3 Jan 77 - 31 Jan 82

6. PERFORMING ORG. REPORT NUMBER:

AUTHOR(s): James R. Aronson

(12)

8. CONTRACT OR GRANT NUMBER(s): DAAG29 77 C 0011; DAAG29 81 C 0010

PERFORMING ORGANIZATION NAME AND ADDRESS:
Arthur D. Little, Inc.
Cambridge, MA 02140

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS:

11. CONTROLLING OFFICE NAME AND ADDRESS:
U. S. Army Research Office
Post Office Box 12211
Research Triangle Park, NC 27709

12. REPORT DATE: Jan 82

13. NUMBER OF PAGES: 47

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office):

LEVEL

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

DTIC ELECTE FEB 1 1 1982 D

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

E

18. SUPPLEMENTARY NOTES

The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

paints	emittance
coatings	camouflage
infrared radiation	optical constants
reflectance	spectra

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report deals with a research program covering an investigation of the use of a theory of the reflectance and emittance of particulate materials as an aid to improving the camouflage properties of various substances. The present contract is a continuation of work pursued under a previous ARO contract (DAAG29 77 C 0011) and a contract with MERADCOM (DAAK70 79 D 0036). The basic problem with which this report is concerned is the development of improved paints or coatings for

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20. ABSTRACT CONTINUED

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MODELING THE INFRARED REFLECTANCE AND EMITTANCE OF PAINTS AND COATINGS

Final Report to
U.S. Army Research Office
Research Triangle Park
North Carolina 27709

by

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Contract DAAG29-81-C-0010

January 1982

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1. INTRODUCTION

This report deals with a research program covering an investigation of the use of a theory of the reflectance and emittance of particulate materials as an aid to improving the camouflage properties of various substances. The present contract is a continuation of work pursued under a previous ARO contract (DAAG29-77-C-0011) and a contract with MERADCOM (DAAK70-79-D-0036).

The original contract with the Army Research Office was principally devoted to modeling of the infrared emittance of fibrous materials. The results of that work were reported in a journal article in Applied Optics in 1979[1]. This work showed that the previously existing theory of the reflectance or emittance of particulate materials could be extended to fibrous materials such as occur in uniforms, tarpaulins, etc. The theory predicts the infrared spectral emittance of a matte of randomly oriented cyclindrical fibers as a function of the optical constants of the fiber material, the fiber diameter, the packing density of the fibers, the packing of the fibers within a fiber bundle, the reflectance of the substrate, and the thickness of the fabric layer. Theoretical simulations were made and compared with experimental measurements of the infrared emittance of polypropylene samples. Both the theory and the experimental data confirmed the validity of the concept that fabrics can be tailored by a proper choice of the above parameters so as to obtain emittances distinctly different from unity. As such, the possibility exists of modifying the thermal signatures of such fabrics so as to aid in their concealment.

In the final year of that contract, the program was redirected toward the development of a theory of the reflectance or emittance of paints and coatings, with the same general purpose of developing the camouflage and concealment technology, but with particular reference to the region of presently existing laser designators and range finders in the near infrared. Dr. Jay Fox, then of MERADCOM, which was a partial sponsor of this early work, suggested that we conduct our modeling experiments using the Army's forest green paint as a candidate system on which to demonstrate the concepts. The results of that study of the visual and near infrared spectrum of forest green painted samples and our modeling are included in this report. At the conclusion of the ARO contract, MERADCOM indicated sufficient interest in the general topic to provide Arthur D. Little, Inc. with a task order contract to continue the work, but this time focusing principally on the thermal infrared region of the spectrum. The results of the MERADCOM work were given in a final report[2] in October 1980. In order to provide continuity for the reader we will quote extensively from the results presented in that report.

The basic problem of interest to the U.S. Army with which this report is concerned, then, is the development of improved paints or coatings for military equipment, particularly in the thermal infrared region but also in the region of the near infrared near 1μm. It is clear that any changes in the formulations of such paints or coatings must be done without deleteriously affecting the visual properties of such materials. The considerable importance of the thermal infrared region, which we will define here as principally the 8-13μm region, but including the 3-5μm region as well has become of continually greater concern owing to the rapid development of thermal imaging systems, such as FLIRs, and other line scanners in which the platform provides the extra dimension for construction of the image. The extreme sensitivity of these devices and their present wide availability, even in the commercial world has dictated that scientists, engineers and paint technologists concerned with these problems devote a considerable amount of effort to improving the camouflage in the thermal infrared region.

Likewise, the development of laser designators and range finders principally in the 1μm region of the spectrum, has mandated improvement in the properties of such paints and coatings in that wavelength region in the sense of greatly decreased reflectance. Reduced reflectance will provide a laser assisted weapon with as little return as possible and so interfere with its effectiveness. This desired goal is in some conflict with the usual goal of concealment of an object by making its properties exactly similar to those of the background in which the object exists. The presumption is made when trying to camouflage against laser designators or range finders that the target has been spotted and the laser assisted weapon needs a sufficient return so as to fix on the target or get an accurate estimate of its range. Regardless of what kind of application in the military world various paints and coatings may have, it is clear that an ability to tailor their properties so as to enable choices to be made would be a valuable aid to camouflage and concealment technology.

The theory being used in our modeling studies was basically developed in previous work[3,4,5], and modified as described in references 1 and 2 for the present application. It is clear that if this theory does indeed accurately simulate the optical properties of painted or coated objects then a great deal of time consuming formulation and test can be avoided as computers can rapidly simulate the reflectance or emittance properties of any surface as a function of the physical and chemical properties of that surface. Our theoretical treatment requires such parameters as the particle size or size distribution, volume fractions of the components, the thickness of the paint or coating layer, the reflectance of the underlying substrate, and particularly the optical constants of the various ingredients of the paint or coating. The optical constants are the real (n) and imaginary (k) parts of the spectral complex index of refraction m, ($m = n-ik$). Here n is the usual refractive index of the material and k is the absorption index related to the Lambert law absorption coefficient α by $k = \alpha\lambda/4\Pi$ where λ is the radiation wavelength.

In one sense, this changes the nature of the problem of predicting the camouflage properties of such materials into one of obtaining the optical constants of the ingredients of the composite. But this, in fact, is a great simplification over an Edisonian approach as the results for any given material can be predicted as a function of the other parameters, even though these may radically change the observable spectrum.

This work has particular value in the infrared region of the spectrum where the experience of paint and color specialists is not widely developed. Unfortunately this is also the region where considerable effort has to be devoted to obtaining optical constants for various materials, as catalogues of such properties are somewhat lacking.

II. THEORY

We began with the theory as presented in references 3, 4, and 5. The most fundamental theoretical changes required were to provide for the occurence of surface reflectance terms originating in the external reflection of the incident beam by the Fresnel relations. It has always been part of our methodology to calculate reflectance rather than emittance as it is intuitively more obvious to most readers as well as to the authors. However, the emittance can be obtained from the reflectance by the use of Kirchhoff's law for opaque substances. That law which is that absorptance equals emittance leads to the formula;

$$\varepsilon = 1-R$$

Where ε is the emittance of the material and R is its reflectance. Both quantities may be subscripted with the angular specifications. That is, the Kirchhoff complement of the reflectance at some angle must be the emittance at that same angle. As reflectance requires two subscripts and emittance only one, analysis shows[6] that emittance may be treated as if the incident beam was coming from inside the medium and entirely diffuse. That is, the proper complement of the emittance at 30° is the reflectance in which the surface is illuminated diffusely (hemispherically) and reflectance is measured at 30° or conversely the surface is illuminated at 30° and the reflectance is measured diffusely.

The surface term R_e in our present formulation refers to the value obtained by integrating the Fresnel relations over all angles, i.e., diffuse reflectance. Associated with this diffuse term for external Fresnel reflectance is an internal term R_i which is equal to

$$R_i = 1 - \frac{(1-R_e)}{n^2}$$

In addition to these surface terms, we also had to derive a formula including the volume reflectance resulting from a finite paint layer on the substrate of reflectance R_g. This formula is:

$$\begin{aligned} R = [&R_e\ (1-R_iR_v)(1-R_vR_g)-R_e(R_v-R_i)(R_v-R_g)e^{-2\gamma x} \\ &+(1-R_e)(1-R_i)R_v(1-R_vR_g)-(1-R_e)(1-R_i)(R_v-R_g)e^{-2\gamma x}] \\ &/[(1-R_iR_v)(1-R_vR_g)-(R_v-R_i)(R_v-R_g)e^{-2\gamma x}] \end{aligned}$$

where x is the thickness of the paint layer, R_v is the volume diffuse reflectance for an infinitely thick layer and $\gamma = (K^2+2KS)^{\frac{1}{2}}$. K and S are the usual absorption and backscattering coefficients given in our previous work[3]. The derivation of this formula is given in reference 2.

Strictly speaking, R_g refers to the reflectance of the underlying substrate as modified by the refractive index of the overcoating layer. However, as the reflectance of metal surfaces are not greatly affected by this consideration, we have used the directly observed reflectance $(1-\varepsilon)$ of our substrate aluminum plate in our calculations thus far. The R_e and R_i for the fine particle theory are calculated from the Lorentz-Lorenz[3] complex index of refraction but in the coarse particle theory we have made the assumption that the only coherent surface terms arise from the matrix, so that these terms are calculated for the matrix material as if it were totally covering the surfaces of the pigment particles. All pigment contributions are included in the volume term.

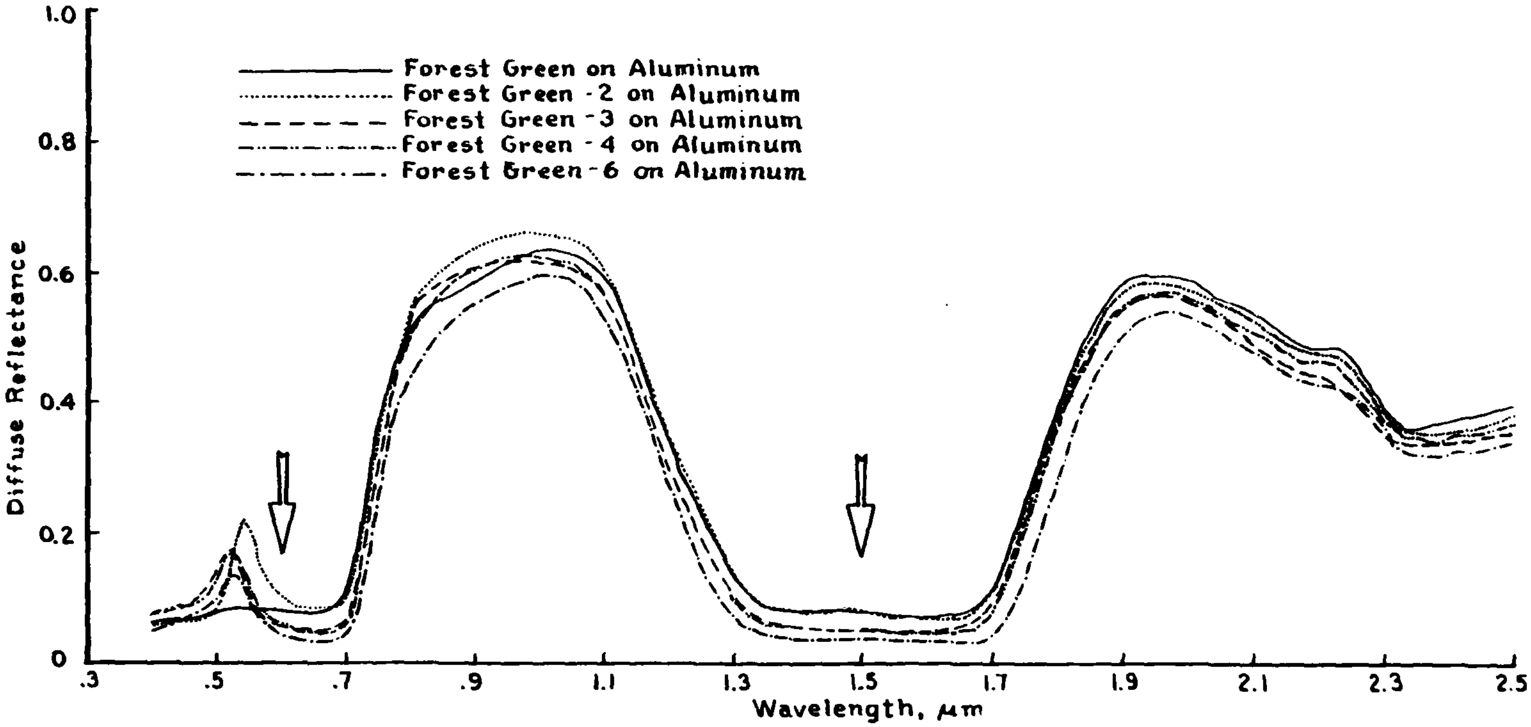
Finally, as our previous theories always assumed particle-vacuum or particle- air interfaces only, the change was made to particle-matrix interfaces by dividing particle complex indices of refraction by the real part of the matrix complex index of refraction. Wavelength dependent effects were likewise adjusted to the index in the medium where necessary.

III. EXPERIMENTAL RESULTS

Table I which is reproduced from the MERADCOM report[2] gives the composition of the forest green paint, and sub formulations that we have chosen to investigate the importance of the various components on the spectral properties of the paint. The simplest overall formulation, FG6 consists only of the alkyd resin and single green pigment, Ferro V-11655. Figure 1 shows the diffuse visible and near infrared spectra of some forest green formulations. It is easily seen that they are almost indistinguishable in the near infrared region of the spectrum. Obviously the various components of the forest green paint were chosen to modify the visual spectrum so as to produce the desired color in this most important region. Nonetheless, insofar as the region of laser designators and range finders near 1μm is concerned, the properties of the sub formulations may be modified with some expectation that the modifications will have the same effects in the forest green system itself. The arrows in the figure indicate regions of strong absorption by the Ferro green pigment, which is the mechanism of diminishing the reflectance below the value of approximately 0.6. It is clearly possible to create a notch in the reflectance spectrum of any of these paints near 1μm by employing a selective absorber in that region. If the absorption is spectrally sharp, it is possible to create a much reduced return from a target, at the same time as not grossly distorting the overall properties in the near infrared region of the spectrum. Possible candidate systems for this, using Fe^{+2} in various inorganic matrices, have been previously suggested by us, but the extent of the absorption and its sharpness would have to be determined in an experimental program. Organic dyes[7] have already been used.

Table 1

Component	Compositions of Forest Green Formulations Volume Fractions in Dry Paint Forest Green MIL-E52798	(Sub Formulations) FG2	FG3	FG4	FG6
1) Acid Insoluble Green Pigment (Ferro V-11655) (Co,Cr,Zn,Ti Spinel)	0.101	0.103	0.106	0.117	0.133
2) Chrome Yellow (med) ($PbCrO_4$)	0.026	0.027	-	-	-
3) Molybdate Orange	0.008	-	-	-	-
4) Cyandur Violet (Carbazole Dioxazine Violet)	0.010	-	-	-	-
5) Talc (Nytal 300)	0.093	0.093	0.097	-	-
6) Diatomaceous Earth (Celite 110)	0.175	0.175	0.183	0.203	-
7) Alkyd Resin (Solids Only) (Beckosol 11-070)	0.587	0.602	0.614	0.680	0.867



DIFFUSE REFLECTANCE OF FOREST GREEN SYSTEM (VISIBLE & NEAR IR)

Figure 1

Figure 2 taken from the MERADCOM report shows the mid-infrared emittance spectra of forest green formulations, and again it is clear that while there are some differences in detail, every forest green sub formulation that we have run has a close to unity emittance in the thermal infrared region (brackets show layer thickness). As pointed out in our MERADCOM report[2], this is due to the absorbing properties of the alkyd binder itself, with the various pigments being less important in determining the overall properties. Figure 3 presents the emittances of the alkyd binder, and a polyurethane binder on aluminum, and our aluminum substrate. We will now show that by using less emitting (absorbing) binders, (Figure 4) one can reduce the overall emittance in the thermal infrared region. While these unpigmented samples would clearly not serve as a camouflage coatings for a target (they simply show the underlving substrate in the visual region), nonetheless the point is clearly demonstrated that both of these substances would serve as an adequate binder. That is, they could serve to hold highly scattering pigments. Having found these more transparent binders which was our priority task, it is now possible to observe that the Ferro green pigment itself is far from ideal. Pigment changes, which would have been ineffective in highly absorbing binders, may now be sought so as to define new paint systems with substantially reduced emittances.

Figure 5 shows measured emittance spectra of two new coatings. These coatings use the Ferro green pigment alone in the two binder systems identified as being suitable for further study. Since polyethylene is not readily soluble it would not be a suitable binder for a conventional paint, but might be used either with modification of application technology (e.g. powder coatings) or as a "stand alone" where a low emittance thermal barrier is desired. Regardless of its ultimate practicality, it is included in this work as the ultimate in thermally transparent organic binders (8-13μm region) so as to provide a standard of comparison for other less thermally ideal candidates. The Kraton* binder (No. G1652) is one of a family of materials that are commercially available block copolymers with a saturated polyolefin

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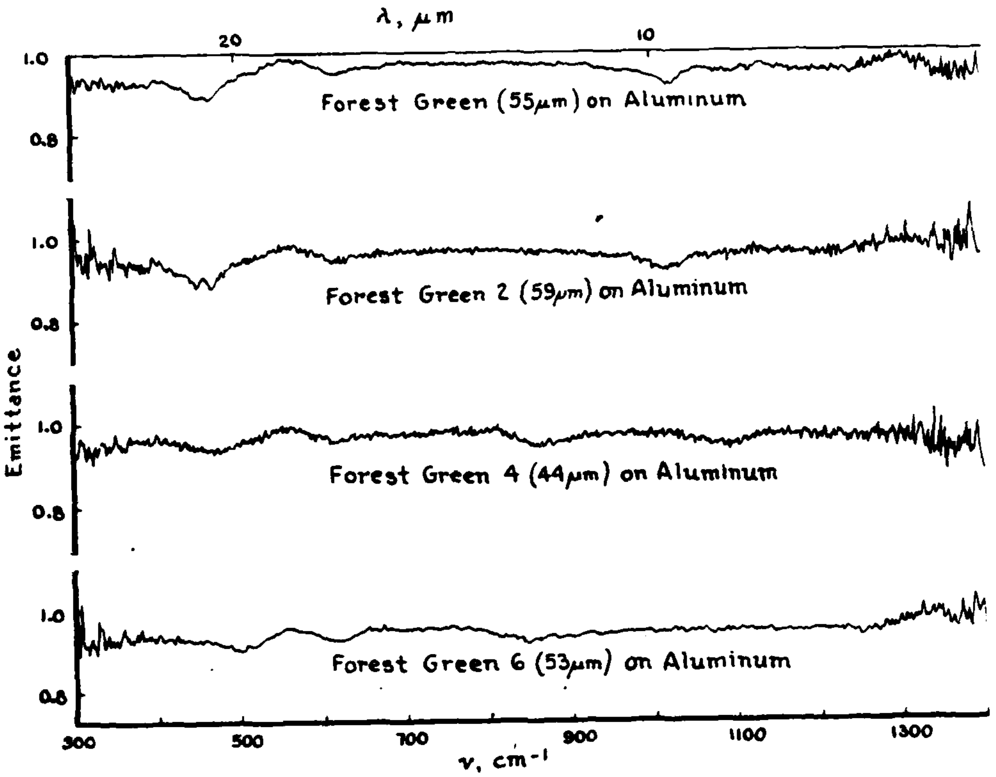
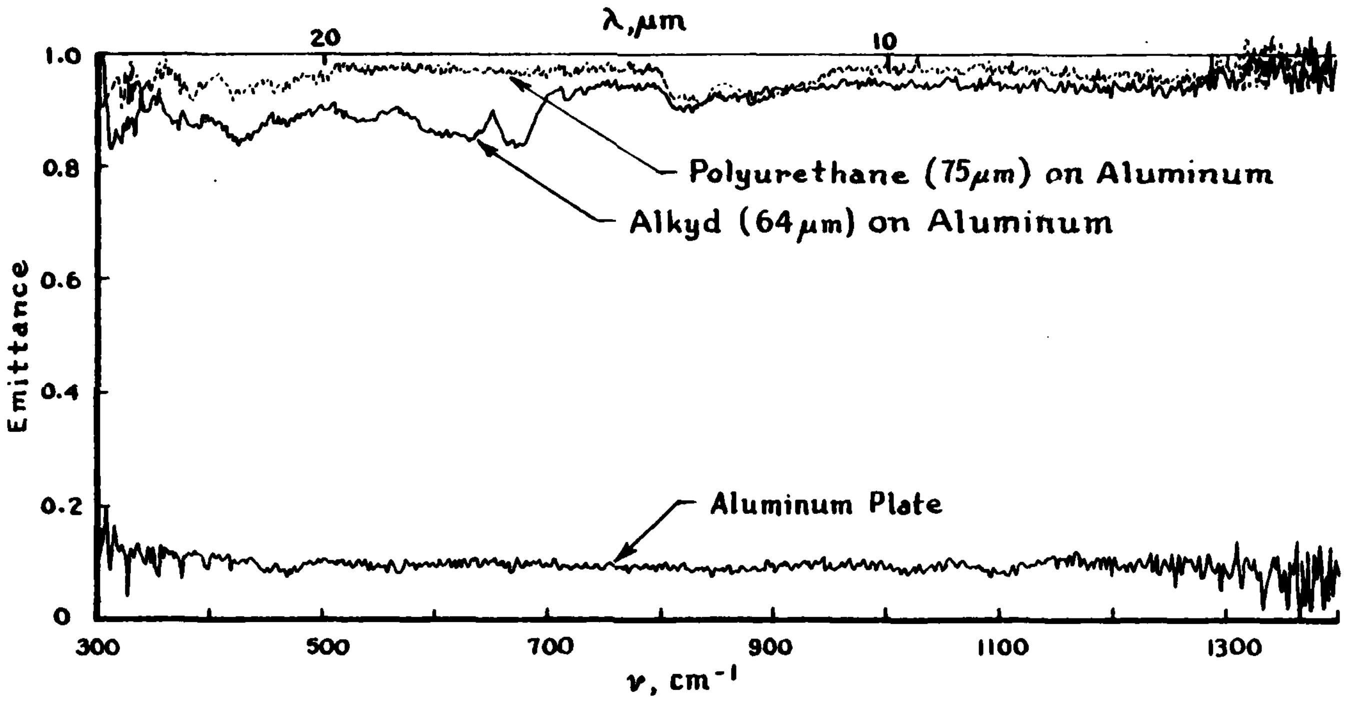
*Shell Chemical Co.



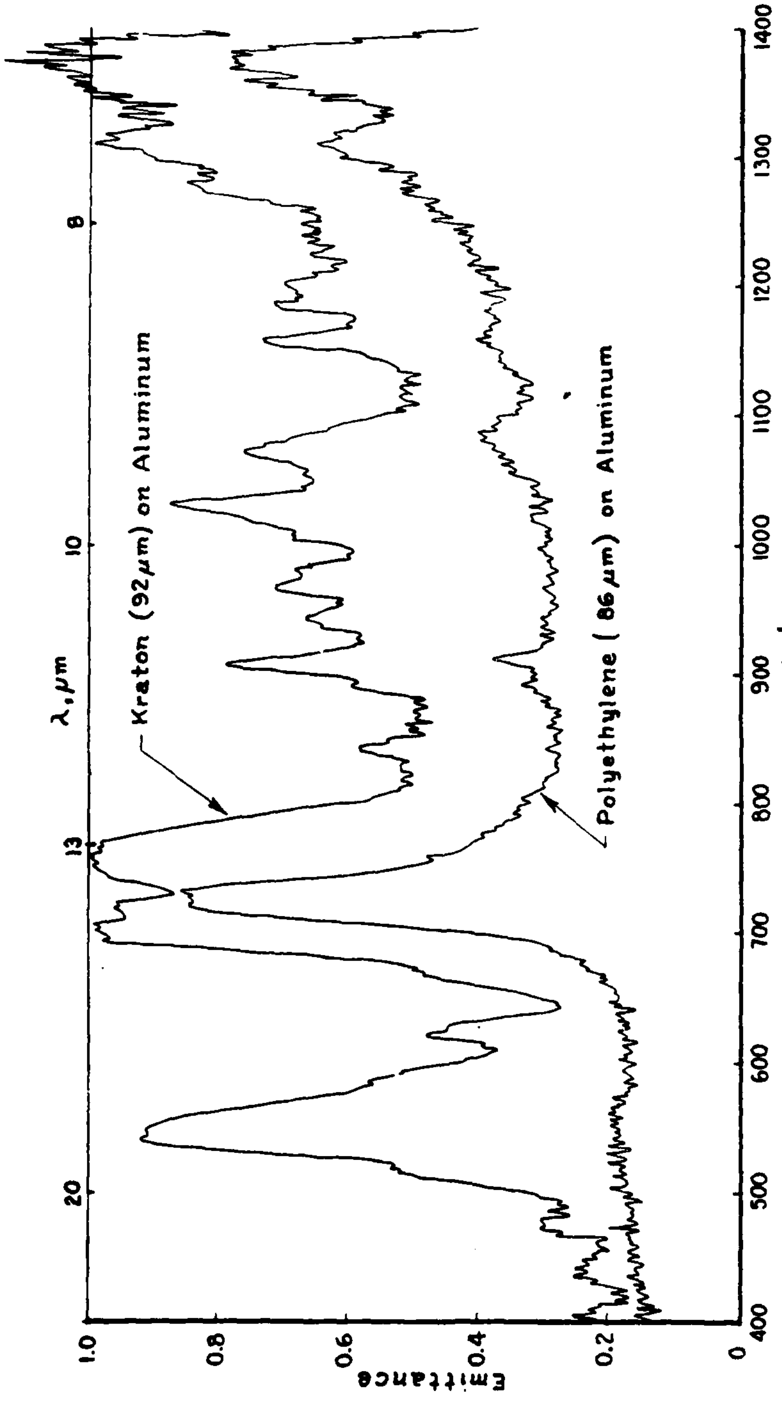
MID IR EMITTANCE SPECTRA OF FOREST GREEN SYSTEM

Figure 2



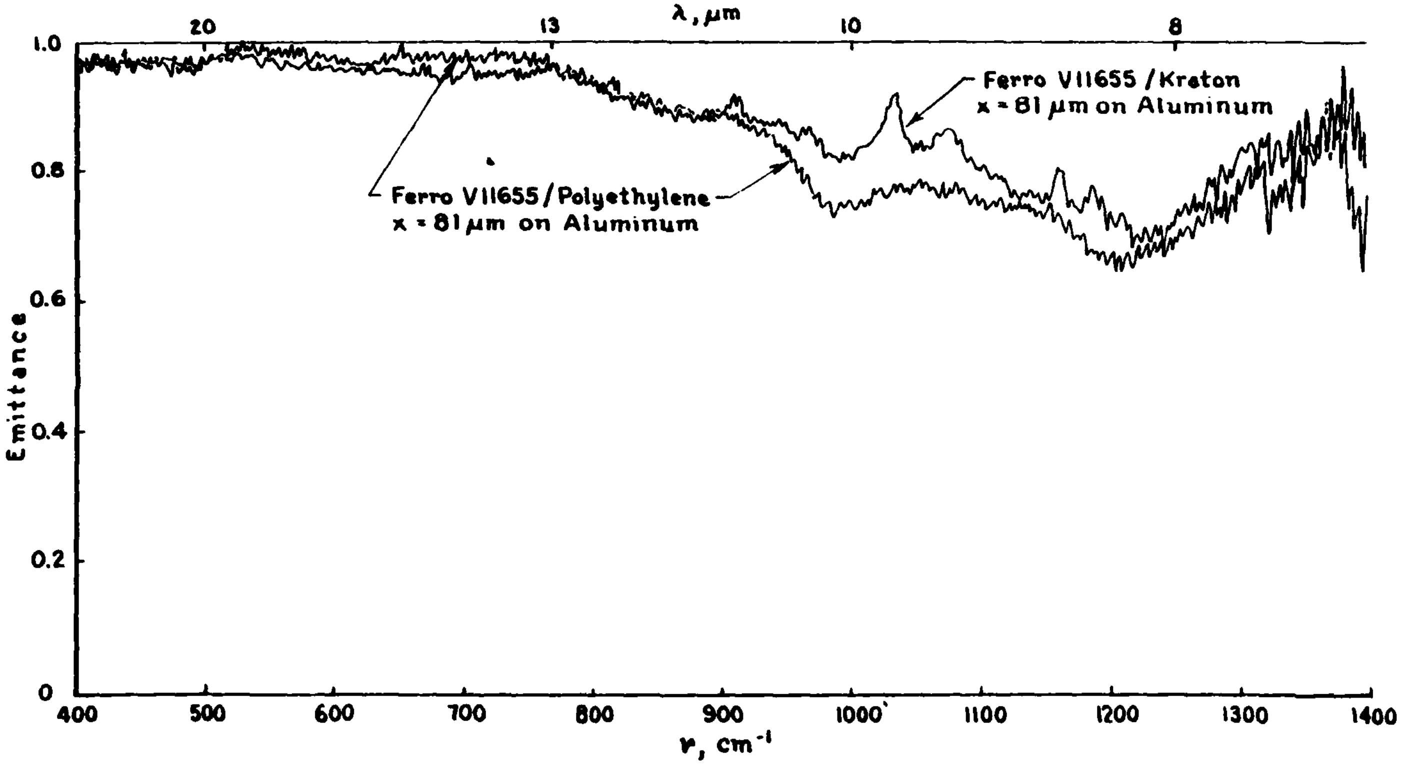
AUXILIARY EMITTANCE DATA

Figure 3



EMITTANCE OF SUGGESTED BINDERS

Figure 4



EMITTANCE SPECTRA OF NEW COATINGS

Figure 5

midblock and polystyrene end blocks. It represents a real paint binder possibility. Figure 4 shows that its emittance is less desirable than the polyethylene but Figure 5 indicates a smaller differential when made into a pigmented coating. As the properties of these coatings now involve a non ideal pigment, it remains to be seen how substantial the loss incurred will be when using Kraton as compared to polyethylene.

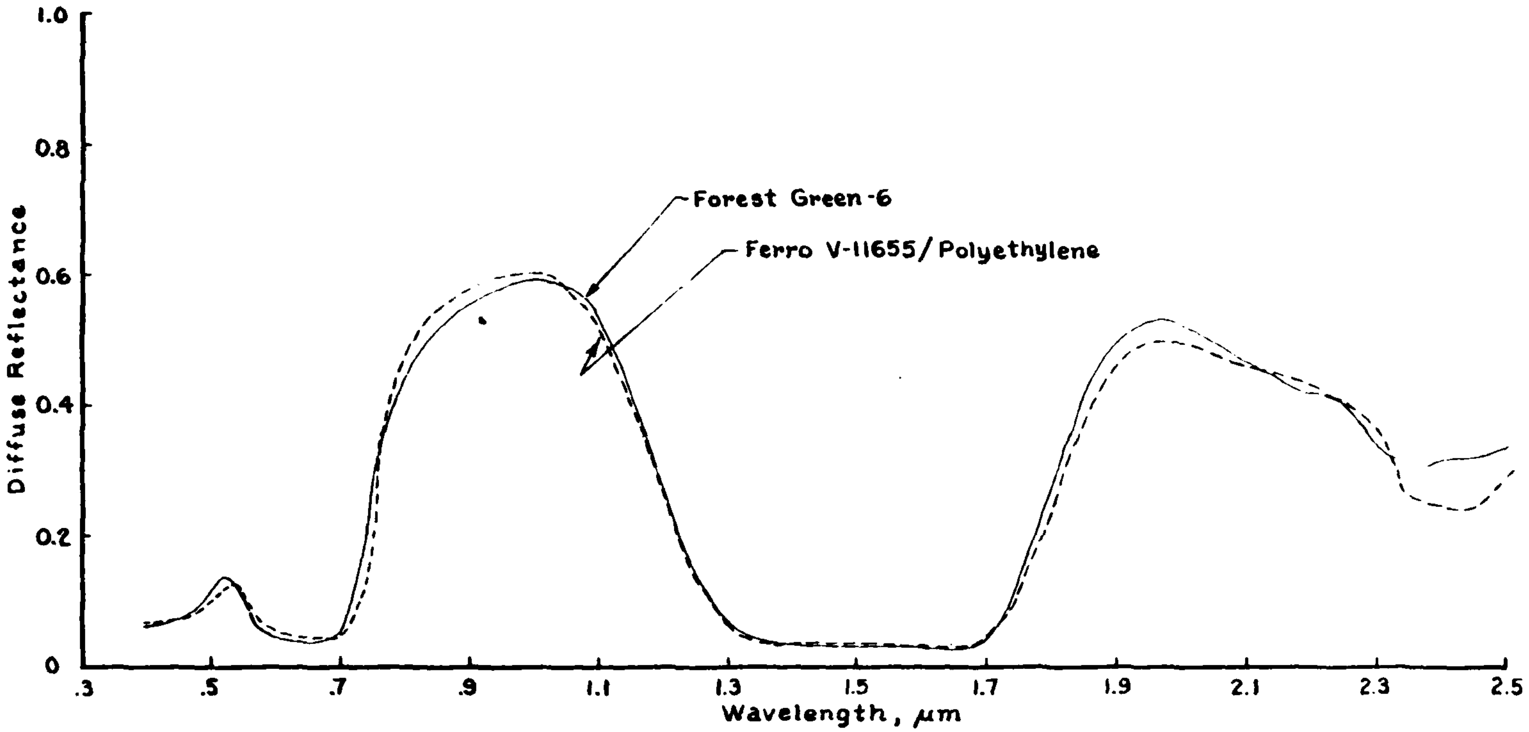
The reason for the insufficient reduction in emittance for these coatings is that the absorption bands of the Ferro pigment while outside the region of immediate interest (8-13μm) are nonetheless sufficiently close spectrally that the tail of the absorption band of the Ferro pigment still has substantial amplitude in the thermal infrared region[2]. Thus it is apparent that the [illegible] choice of a substitute green pigment would be one whose principal infrared absorption bands are well removed from the 8-13μm region.

Figure 6 demonstrates that the modification of the thermal emittance by changing binders does not affect the visible or near infrared spectra in any significant way. This was to be expected as the binder only provides a transparent medium with refractive index near 1.5 that serves to contain the absorbing and scattering pigments.

IV. OPTICAL CONSTANTS (COMPLEX REFRACTIVE INDICES)

A. Visible and Near Infrared Regions

As it was concluded at the early part of our previous contract that the Ferro green pigment was the most important component of the forest green paint system, it became exceedingly important to obtain optical constants for this material. A sample of this pigment was obtained from Mr. Aladar Burgyan of the Ferro Corporation and hot pressed in our laboratories to form a homogeneous material. This sample was polished and its reflectance measured with our Beckman DK 1A spectrometer. It was apparent from the data that the absorption index k is too



DIFFUSE REFLECTANCE OF MODIFIED BINDER COATING (VISIBLE & NEAR IR)

Figure 6

small to significantly influence the reflection spectrum in the visible and near infrared regions and so only the real part n of the refractive index could be obtained by reducing our data. The refractive index of this material as obtained from the visible and near infrared data is given in Table 2.

A qualitative technique, that of measuring the transmission of thallium chloride pellets of this pigment was used in order to try and obtain some information relative to the absorption index. Thallium chloride was chosen owing to its refractive index (2.25) being close to that of the green pigment so as to minimize scattering. Broad absorption bands were found centered near 0.6 and 1.5μm; each band is a doublet. Peak values of k near 0.015 were obtained.

An attempt to hot press and thus reduce data from the chrome yellow in a manner similar to that used for the Ferro green pigment failed as chemical deterioration took place. It was therefore decided to obtain optical constants for chrome yellow from the mineral crocoite which was obtained from Carl Francis, curator of the Harvard University collection. The data are given in Table 3.

A sample of the diatomaceous earth (cellite 110) used in the forest green system was obtained and a potassium bromide pellet of it was measured. The pellet showed essentially zero absorption index. The visible range value for opal[8] of $n = 1.44$, was used for this material in our visible and near infrared computer simulations. Some difficulty was encountered obtaining a good film of the alkyd resin binder, but the best film obtained was used to make transmission measurements and small bands were observed in the visible and near infrared region. These have peak values of k less than 5×10^{-4}. Therefore for our computer simulation we decided to set the absorption index equal to zero for the binder and use the value of $n = 1.54$ obtained by Brewster angle measurements made in our laboratory.

TABLE 2

Ferro Pigment V-11655

λ,nm(VIS)	n	λ,nm(NIR)	n
400	2.01		
500	1.94		
590*	1.91		
600	1.90		
700	1.90		1.92
800	1.89		
		900	1.84
		1100	1.79
		1300	1.81
		1500	1.85
		1700	1.93
		1900	1.93
		2100	1.95
		2300	1.98
		2500	2.00

*At the sodium D lines an independent measurement was made by a Brewster angle measurement. The value obtained was 2.18±.04 suggesting sufficient error in the above data that the observed wavelength variations may not be real.

TABLE 3 - CROCOITE+

λ, nm	n
400	2.33
500	2.44
590*	2.29
600	2.30
700	2.31
800	2.23
900	2.23
1100	2.14
1300	2.13
1500	2.13
1700	2.12
1900	2.09
2100	2.13
2300	2.11
2500	2.10

*The Brewster angle derived sodium D lines value is 2.08.

+X-ray examination of the crystal face used shows it to be about 9° off the 200 plane.

B. Thermal Infrared Region

As the emphasis of our work shifted from the visible and near infrared regions of the spectrum to the thermal infrared region, it became obvious that more adequate sets of optical constants were needed. For the derivation of such optical constants, we would rely on the reflectance method developed in our previous work[9] providing that the optical constants were in the range for which strong reflection bands develop i.e., regions of strong absorption. In the infrared region of the spectrum, this is generally true for inorganic materials. Our results for the inorganic pigments involved in this study were given in our previous report.[2] However the organic materials desired as binders have sufficiently weak absorption (even though in most cases, too strong to be suitable for paint binders) that the reflection method could not succeed. We therefore developed a new method based on Brewster angle transmission measurements.

The Brewster angle, ϕ is defined by n = tan ϕ , where n is the refractive index of the medium. At the angle of incidence ϕ, radiation whose electric vector is in the plane of incidence cannot be reflected. Thus for this particular angle, and with the use of a polarizer that passes only such radiation, the reflection loss will be zero. That being true, the usual law for thick samples (without interference phenomena)

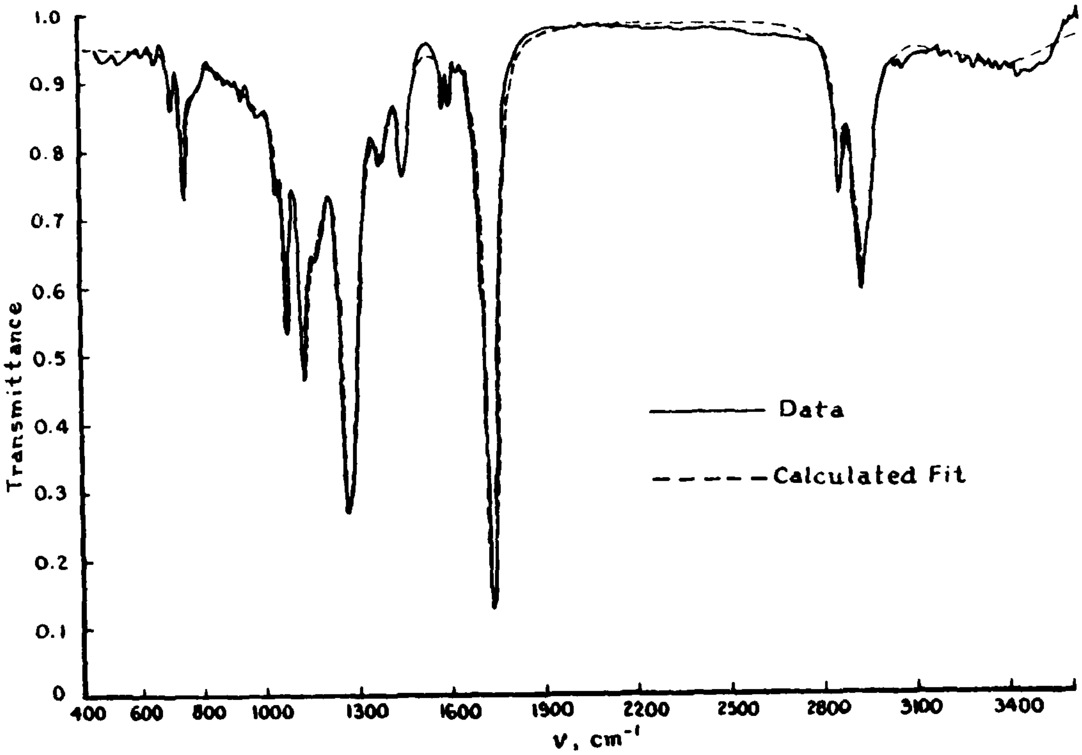
$$T = \frac{(1-R)^2 e^{-\alpha x}}{1-R^2 e^{-2\alpha x}}$$

is simplified to $T = e^{-\alpha x}$. Therefore it is possible to reduce problems involving a least squares fit to the reflection losses, where the reflectance is from an imperfect surface.

A program was written to carry out the least squares type analysis previously used[9] to obtain the Lorentz line parameters and hence the optical constants from such transmission data. This program was first used during our previous work[2] to obtain optical constants for the alkyd resin in present use as a paint binder. The results are reproduced in Figure 7 and Table 4 gives the derived Lorentz line parameters.

The same method has now been used for the two materials suggested as future binders. These materials were both chosen for their relative transparency in the 8-13μm region. The first, polyethylene, as already discussed would be difficult to make into a conventional paint binder. Figure 8 shows the transmission spectrum obtained on our Digilab FTS 15-C instrument together with the fit obtained by our Brewster angle Lorentz line method. Although we obtained data over a much broader range of frequencies, we chose to reduce the data to Lorentz line parameters only in the spectral region between about 600 and 1500 cm^{-1}. The fit using 14 lines (Table 5) can be seen to be quite good although several small features were not considered worth fitting. At about 730 cm^{-1} and 1470 cm^{-1} the transmittance is essentially zero so that a large fitting error at these frequencies is possible. However, as both of these peaks are outside the range of interest, these results were accepted. Clearly if it was important, further work could be done to both better fit the data at the peaks of these lines and to fit the further data we have at higher frequencies.

A 16 line fit to the Kraton film obtained by the same techniques is shown in Figure 9. Once again the data were obtained over a much broader spectral range than used for our present purposes and the same comments as made for the polyethylene film apply here as well. Arbitrarily good fits can be obtained if further very small lines are used and higher sampling density along the transmission curve is taken. Table 6 give the Lorentz line parameters for this Kraton film. It can easily be seen from the strengths S_j of the lines in these tables that the two new suggested binder materials indeed are much weaker absorbers overall than is the alkyd resin. The strength of these bands indicates the strengths of the absorption coefficients in the region in question, and thus an order of magnitude and more improvement can be seen in the 8-13μm region.



LORENTZ LINE FIT TO ALKYD RESIN TRANSMITTANCE

Figure 7

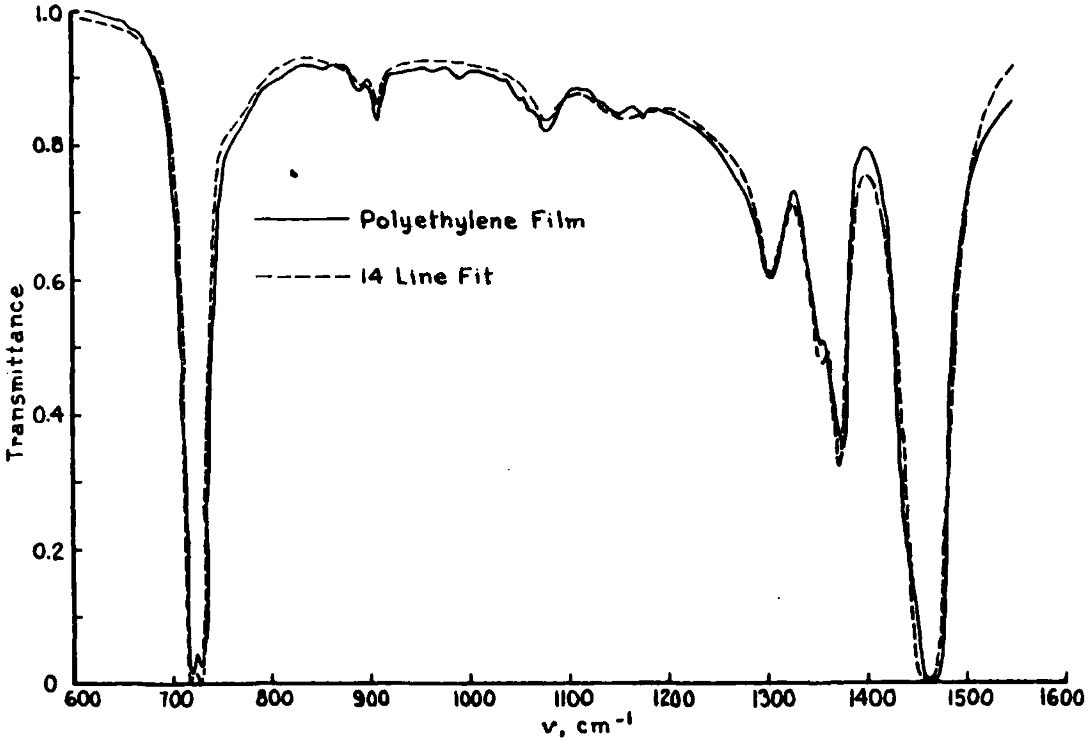
Table 4

Alkyd Film

Estimated standard deviations are given in parentheses

$\varepsilon_\infty = 2.3716$

j	ν_j		S_j		γ_j	
1	3360.35	(7.23)	1.693E-03	(7.872E-05)	0.13555	(0.00785)
2	2932.26	(0.64)	1.807E-03	(4.305E-05)	0.02259	(0.00071)
3	2856.83	(0.66)	3.043E-04	(2.309E-05)	0.00764	(0.00073)
4	1730.94	(0.19)	9.787E-03	(1.149E-04)	0.01604	(0.00033)
5	1599.37	(1.21)	1.928E-04	(4.654E-05)	0.00736	(0.00231)
6	1580.26	(0.91)	1.612E-04	(4.033E-05)	0.00530	(0.00167)
7	1456.20	(0.89)	1.500E-03	(1.037E-04)	0.02203	(0.00192)
8	1387.16	(1.45)	1.408E-03	(1.456E-04)	0.02842	(0.00362)
9	1273.28	(0.33)	2.058E-02	(2.996E-04)	0.04097	(0.00087)
10	1175.07	(1.64)	3.514E-03	(5.132E-04)	0.03691	(0.00483)
11	1128.39	(0.57)	1.007E-02	(5.885E-04)	0.03390	(0.00192)
12	1071.62	(0.40)	4.151E-03	(2.816E-04)	0.01778	(0.00135)
13	1041.27	(1.14)	1.099E-03	(2.974E-04)	0.01676	(0.00440)
14	976.50	(11.97)	9.532E-03	(2.247E-03)	0.20333	(0.04350)
15	469.96	(240.55)	1.326E-01	(1.468E-08)	2.29674	(1.14656)
16	781.88	(5.64)	2.258E-03	(9.357E-04)	0.06652	(0.02646)
17	743.68	(0.52)	3.950E-03	(4.509E-04)	0.02177	(0.00259)
18	704.56	(1.13)	1.046E-03	(2.456E-04)	0.01658	(0.00495)



LORENTZ LINE FIT TO POLYETHYLENE FILM TRANSMITTANCE
Figure 8

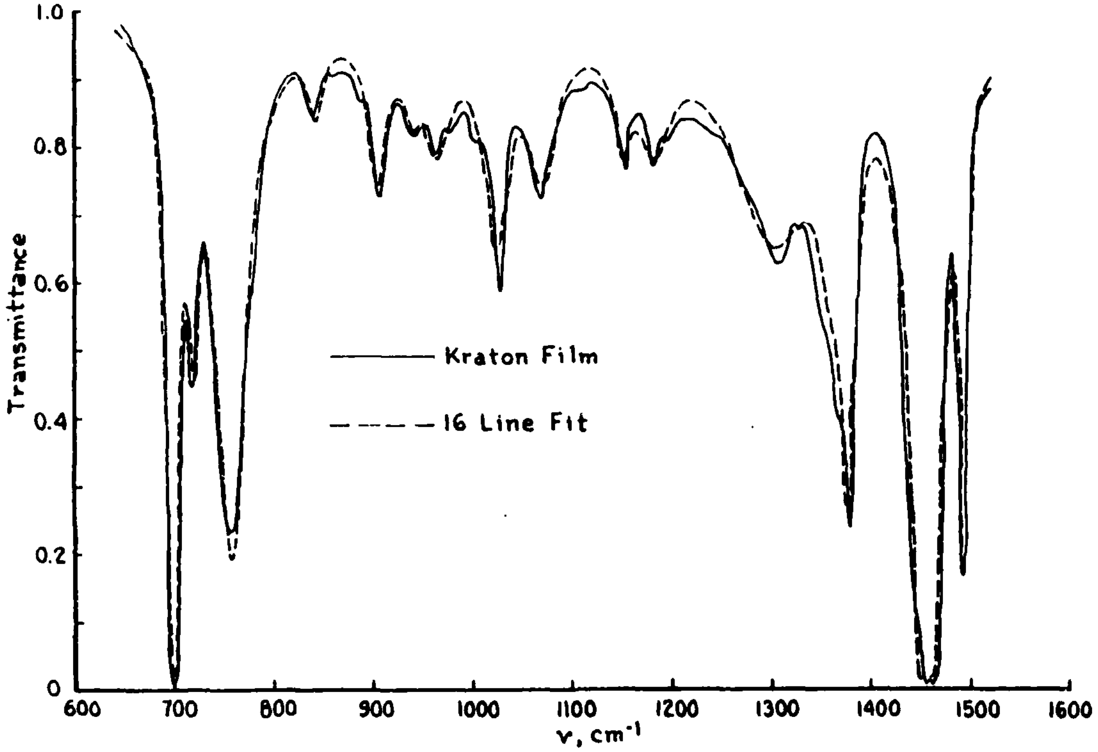
Table 5

Polyethylene Film

Estimated standard deviations are given in parentheses

ε_∞ 2.2801

j	ν_j		S_j		γ_j	
1	1458.99	(0.31)	1.684E-03	(2.933E-04)	0.01003	(0.00211)
2	1373.04	(0.58)	1.421E-04	(2.228E-05)	0.01000	(0.00139)
3	1352.95	(1.49)	1.576E-04	(3.396E-05)	0.01871	(0.00357)
4	1303.87	(1.58)	1.641E-04	(6.685E-05)	0.02727	(0.00696)
5	1257.22	(15.85)	1.781E-04	(1.764E-04)	0.07686	(0.05334)
6	1157.44	(9.84)	2.006E-04	(1.558E-04)	0.08736	(0.04360)
7	1078.59	(4.29)	7.309E-05	(8.209E-05)	0.03617	(0.02477)
8	1015.05	(57.10)	1.405E-04	(5.111E-04)	0.15352	(0.38519)
9	908.06	(1.37)	1.759E-05	(1.173E-05)	0.00924	(0.00599)
10	893.87	(30.52)	2.371E-04	(3.816E-04)	0.15139	(0.17269)
11	889.90	(4.17)	6.665E-06	(1.541E-05)	0.01022	(0.02068)
12	770.85	(5.77)	2.429E-04	(1.313E-04)	0.07799	(0.03553)
13	728.57	(0.57)	2.117E-03	(1.804E-03)	0.00498	(0.00536)
14	719.28	(0.76)	2.347E-03	(2.263E-03)	0.00456	(0.00411)



LORENTZ LINE FIT TO KRATON (29% POLYSTYRENE) TRANSMITTANCE

Figure 9

Table 6

Kraton Film

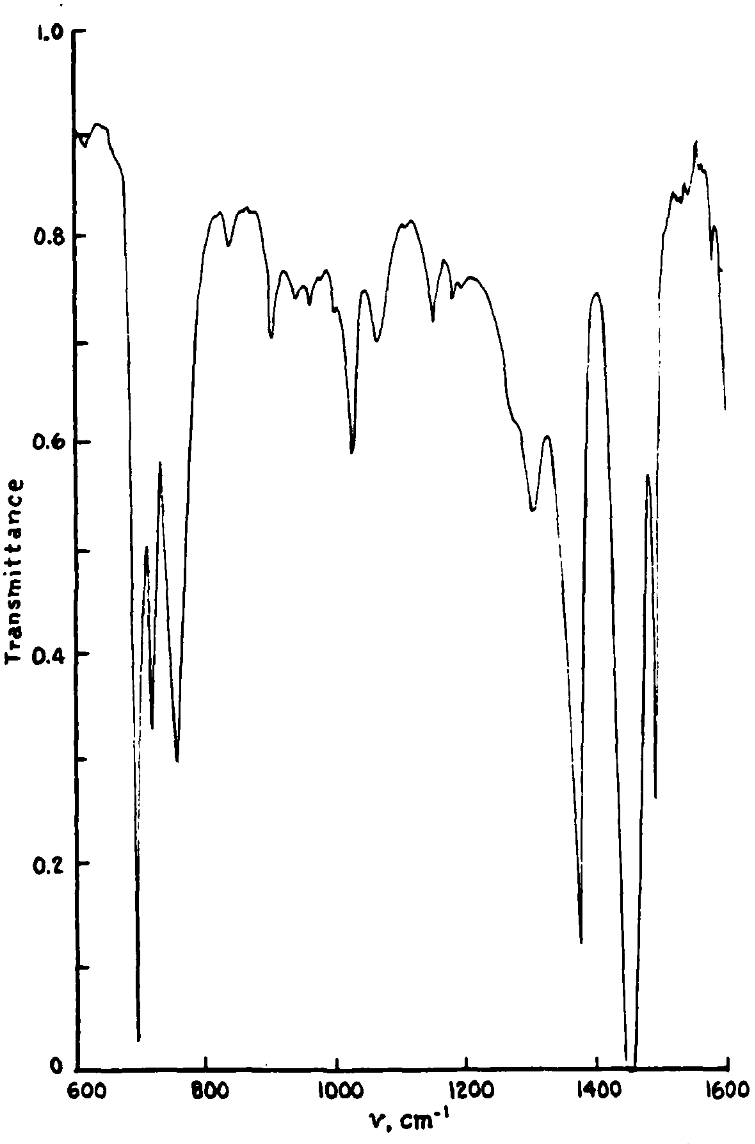
Estimated standard deviations are given in parentheses

ε_∞ =2.3600

j	ν_j		S_j		γ_j	
1	1493.10	(0.18)	2.340E-04	(1.891E-05)	0.00373	(0.00037)
2	1453.71	(1.40)	1.689E-02	(1.601E-02)	0.00124	(0.00124)
3	1376.83	(0.65)	4.523E-04	(1.158E-04)	0.00886	(0.00179)
4	1360.10	(4.98)	2.947E-04	(2.150E-04)	0.02101	(0.01060)
5	1302.72	(4.38)	1.291E-03	(1.976E-04)	0.06968	(0.00942)
6	1184.45	(3.58)	2.773E-04	(9.913E-05)	0.03052	(0.01047)
7	1152.62	(2.61)	1.441E-04	(6.768E-05)	0.01804	(0.00785)
8	1071.17	(1.95)	4.357E-04	(7.042E-05)	0.03142	(0.00597)
9	1025.42	(1.17)	5.761E-04	(8.429E-05)	0.02557	(0.00425)
10	966.36	(3.73)	4.321E-04	(1.611E-04)	0.03588	(0.01277)
11	940.89	(3.32)	1.087E-04	(1.093E-04)	0.01666	(0.01449)
12	906.65	(1.38)	4.125E-04	(6.508E-05)	0.02412	(0.00489)
13	842.52	(2.35)	1.817E-05	(5.185E-05)	0.02135	(0.00833)
14	757.32	(0.48)	4.581E-03	(1.569E-04)	0.03483	(0.00190)
15	720.26	(0.53)	6.011E-04	(9.657E-05)	0.01349	(0.00259)
16	699.50	(0.52)	1.103E-02	(1.098E-02)	0.00278	(0.00295)

The Kraton material used here (No. G1652) is made by Shell and contains about 29% polystyrene by weight. A comparison of the spectra of the two films indicates that the polyethylene type bands and the polystyrene type bands can both be seen in the Kraton material. Another material in the Kraton series of polymers that contains still less of the polystyrene bands is obtainable from Shell. As the strong polyethylene bands are principally outside of the 8-13μm region, the less polystyrene in the Kraton film used, the better will be its optical properties in that region. A second Kraton film (No. G1657) containing only 14% polystyrene by weight was also run (Figure 10) but not reduced as it cannot have as low absorption as the polyethylene, having an intermediate behavior between the polyethylene and the first Kraton film used. If necessary these data could also be reduced to optical constants although this polymer is softer and would be expected to be less durable.

For the purpose of theoretical simulations of a variety of prospective paint or coating mixtures, we obtained Lorentz line parameters and hence optical constants for a number of possible pigments from the literature. This is part of a long-standing effort that we have been carrying out to obtain the optical constants of as many materials as possible in the infrared spectral region. Lorentz line parameters for materials of possible interest in this work such as Fe_2O_3[10],CdS[11] Cr_2O_3[12] $CaCO_3$[13] ZnO[14] and Rutile[15] were added to our computer file. The quality of the values obtained from the literature is somewhat variable but at least these data provide us with an extended data base.



TRANSMITTANCE OF KRATON (14% POLYSTYRENE) FILM
Figure 10

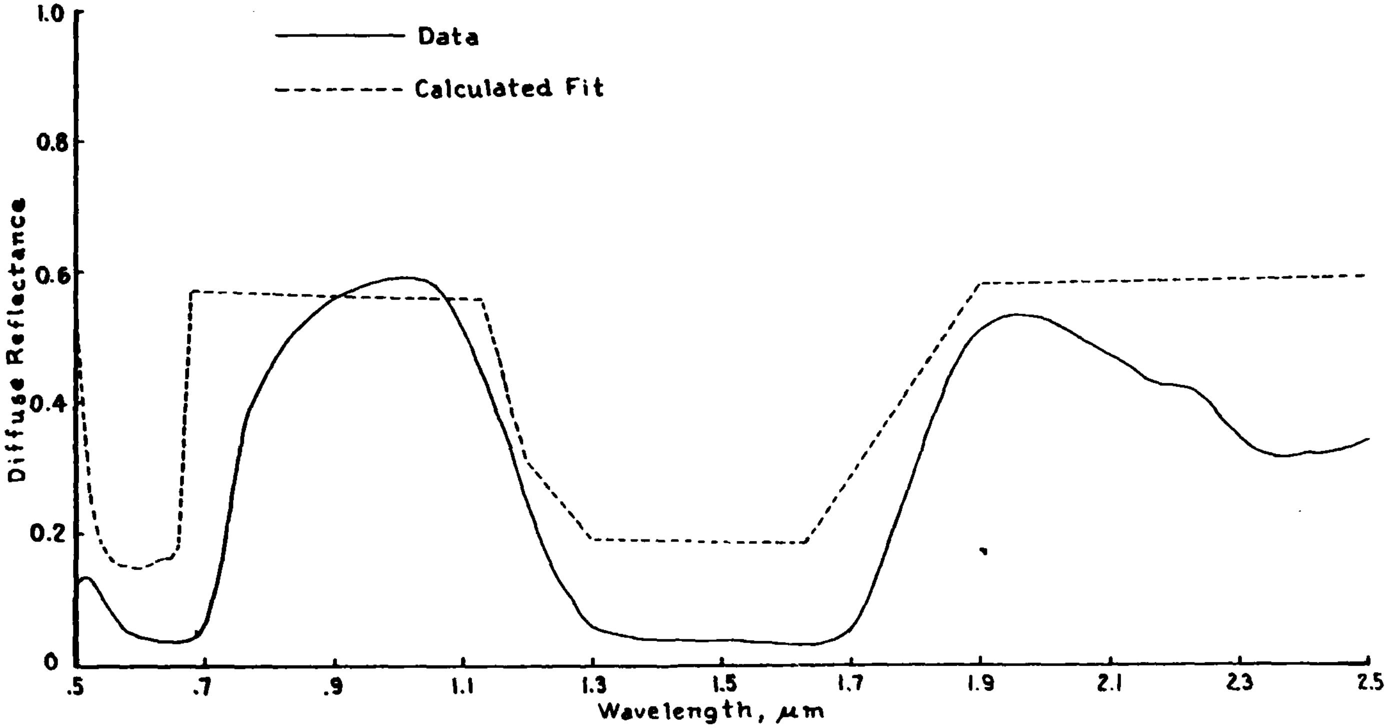
V. COMPARISON OF EXPERIMENTAL RESULTS WITH THEORETICAL SIMULATIONS

A. Visible and Near Infrared Spectra

Our first computer simulation (during our previous ARO contract) in the visible and near infrared region was made using the three component system, alkyd resin, Ferro green pigment and diatomaceous earth (FG 4).

The reflectance of the aluminum substrate (approximately 0.55) and the thickness of the paint layer (80µm) were measured and used as values for our modeling. The absorption data were reduced to k values at 29 spectral points and these were used in the simulation of the reflectance spectrum from 0.5 to 2.5µm. The results are shown in Figure 11. While many more points could have been processed it was decided owing to the qualitative nature of some of the input data, that this number of points would sufficiently represent the spectrum to establish whether our computer simulation indeed adequately represents the experimental measurements.

The results shown in the figure indicate that the principal features of experimental spectrum are adequately reproduced by the theoretical treatment, with the main deficiency being a reflectance level that is higher than measured in the regions of low reflectance. At those spectral points where the k of the pigments was taken to be zero, an obvious under estimate, a plateau appeared on the reflection bands at approximately the correct reflectance level, indicating that the simulation is reasonable. Clearly any value of the absorption index different from zero will make some difference in this region and thus remove the very flat appearance of the spectrum. The fit is reasonably good, considering the number of approximations made and the paucity of points. The reflectance level obtained from the ca. 80µm thick layer is quite similar to that obtained from the substrate, at the peaks of both near infrared reflectance bands. This results from the near zero extinction



COMPUTER SIMULATION OF VISIBLE AND NEAR INFRARED SPECTRUM OF FG4 (29 DATA POINTS)

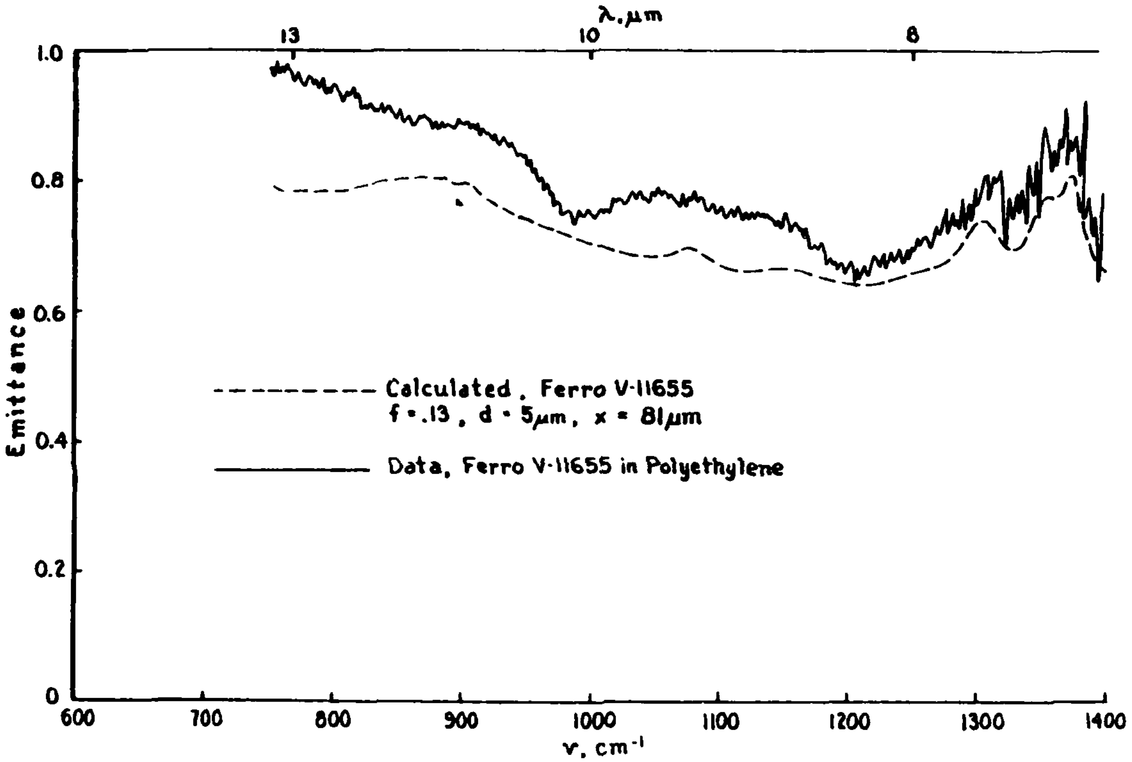
Figure 11

of the pigments at these wavelengths. Thus it is apparent that the way to reduce the reflectance at any wavelength would be to incorporate into the paint, material with specific absorption at that wavelength. The incorporation of a ferrous iron containing compound could thus be expected to create a notch in the 1.1μm region as do certain infrared dyes.

B. Thermal Infrared Spectra

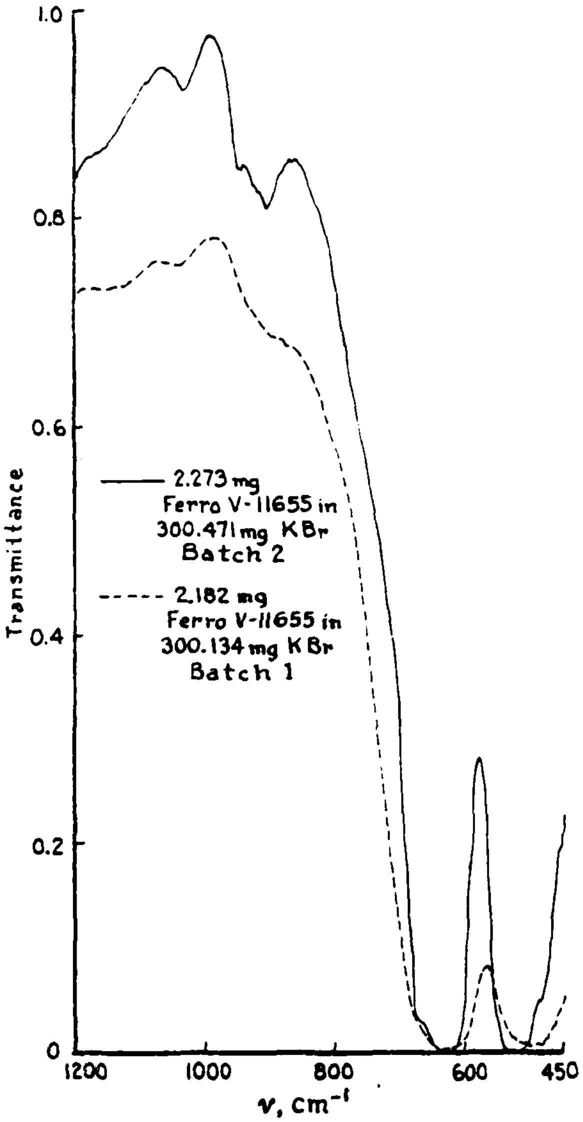
A comparison of the experimental emission spectrum of the polyethylene pigmented with the Ferro green pigment and the theoretical simulation is shown in Figure 12. The parameters of the simulation, d, the particle diameter, x the layer thickness and f the volume fraction taken from the experimental sample are given in the figure. The general level and shape of the spectrum can be seen to be in reasonable agreement with the experimental data but there are significant discrepancies in an experimental minimum in the emittance spectrum near 980 cm^{-1} and greater emission at the long wavelength end of the spectrum. A run made with a new batch of the same green pigment accentuated these problems while adding another minimum near 850 cm^{-1} that is not predicted by the theoretical simulation. As these results were most mysterious, a set of analytical experiments were carried out on the two batches of the green pigment. The characteristics, mentioned above, of the discrepancy of the experimental data from theoretical simulations were traced by analytical experiments to very small bands in the green pigment which in fact were much more pronounced in the new batch of the green pigment.

Several discussions were held with Mr. Burgyan of the Ferro Corp relative to the origin of these bands but no satisfactory explanation was obtained. It is clear however, from the results shown in Figure 13 (transmission spectra of potassium bromide micropellets containing samples from the two different batches of the green pigment) that the bands causing the discrepancies from theory were indeed variable between the two batches, although it can be seen that they existed to some extent in the original batch. An examination of the data in the MERADCOM



COMPUTER SIMULATION AND EXPERIMENTAL DATA FERRO V-11655 IN POLYETHYLENE

Figure 12



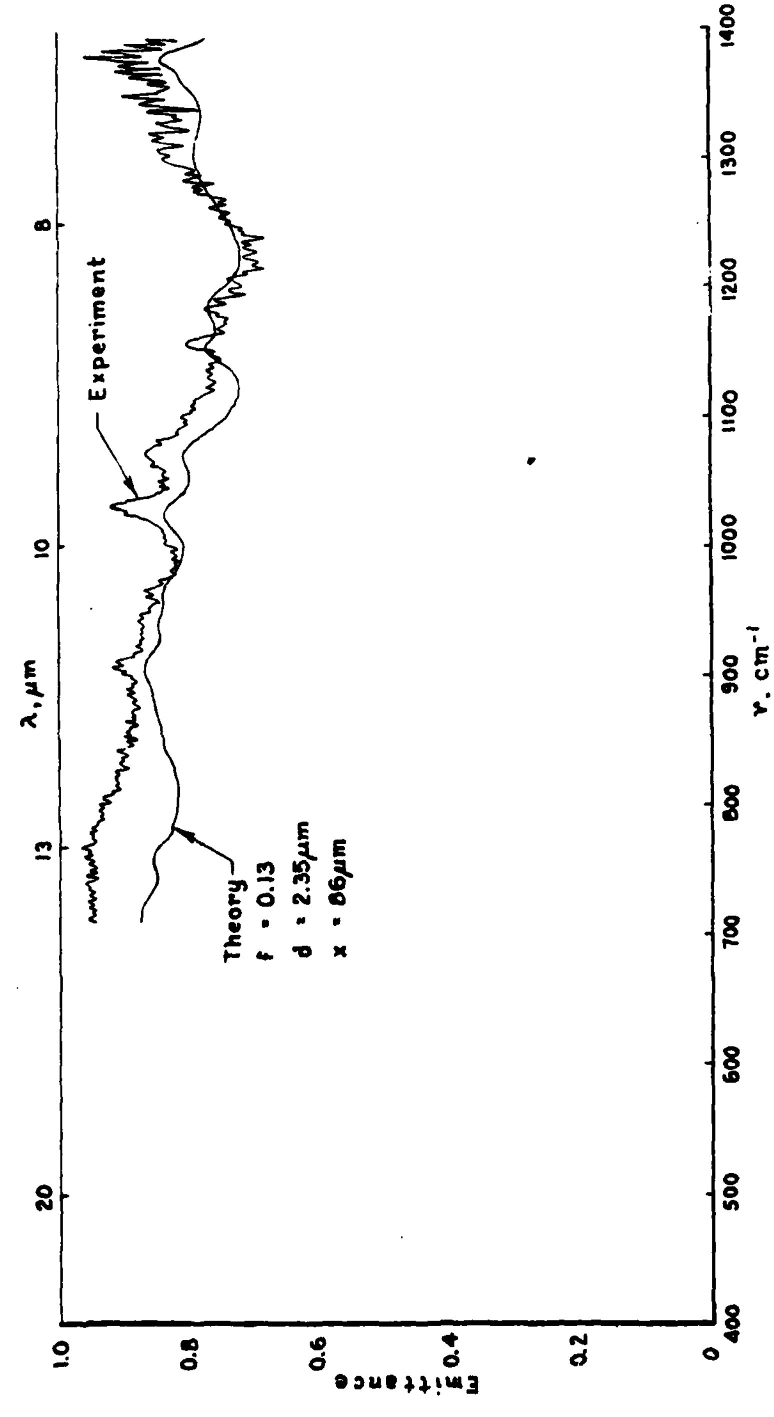
ANALYTICAL PELLET TRANSMISSION SPECTRA SHOWING THE VARIABILITY OF THE SMALL ABSORPTION FEATURES CAUSING DEFECTIVE OPTICAL CONSTANTS

Figure 13

report) from which the optical constants of the green pigment were obtained, indicates that exceedingly small bands at the appropriate wavelengths may be seen. These bands were so small that we did not originally attempt to fit them, so the optical constants derived and used for our simulation experiment were deficient in this regard. As the second batch of the green pigment showed distinctly greater concentration of the materials causing these bands, a new hot pressed sample was made and polished, and an attempt made to derive the optical constants. Unfortunately the bands causing these features are so small, that we were unable to obtain satisfactory optical constants representing them by the reflection method. The proper method would be to make transmission measurements and combine the two techniques.

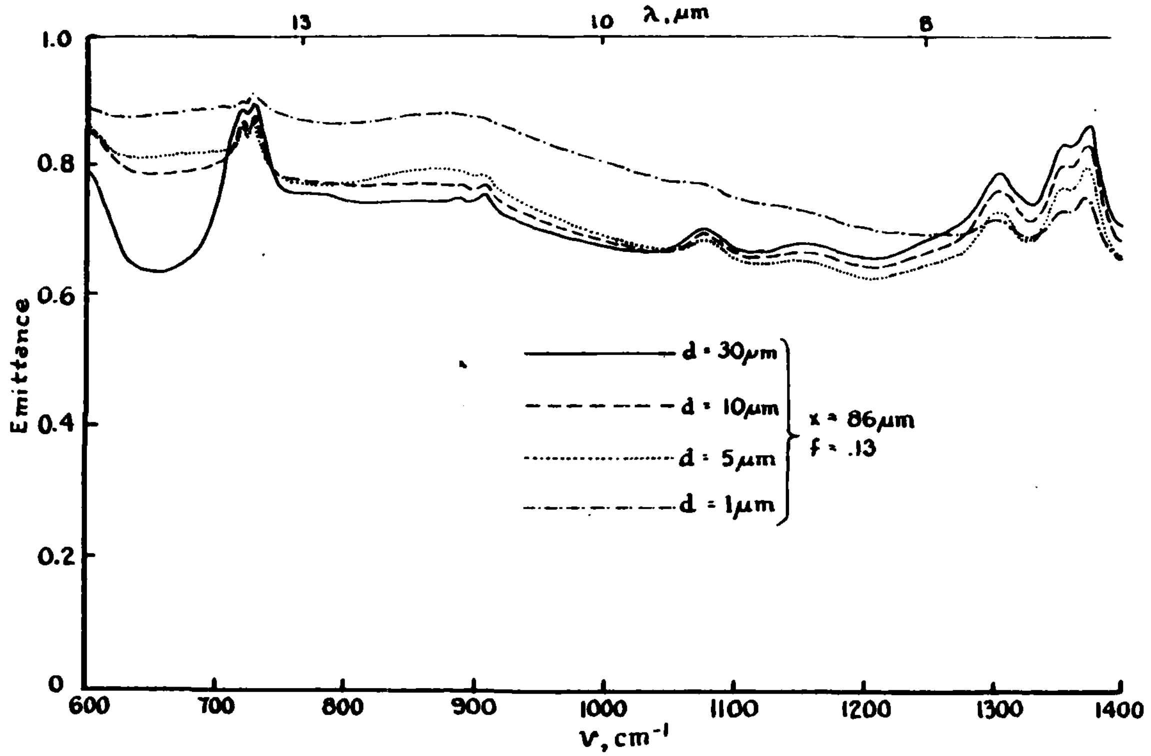
A similar comparison of the green pigment in the Kraton binder is shown in Figure 14. As before, the relatively minor discrepancies are traceable to optical constants that are not entirely adequate for the purposes, but the general overall level of the predicted spectrum agrees adequately well with the theoretical simulation. It is clear that as the highest experimental emittances were obtained at the lowest frequency portion of the spectrum, the principal difficulty in obtaining sufficiently low emittance in the 8-13μm region is the close spectral proximity[2] of the absorption bands of the green pigment. We therefore feel that the theoretical simulation provides an adequate representation of the gross level of the emittance spectrum as well as sufficient detail such that we can use it as an adequate estimator of the performance of future systems.

With this in mind, a number of theoretical simulations were carried out using those optical constants we have been able to obtain either from the literature or from our work. Figure 15 shows the effect of the particle size on the emittance spectrum in the system consisting of polyethylene and the Ferro green pigment alone. The peaks near 720 cm^{-1} may be overemphasized owing to difficulties in fitting the transmittance data near zero transmittance as shown in Figure 8. This kind of



COMPUTER SIMULATION AND EXPERIMENTAL DATA FERRO V-11655 IN KRATON

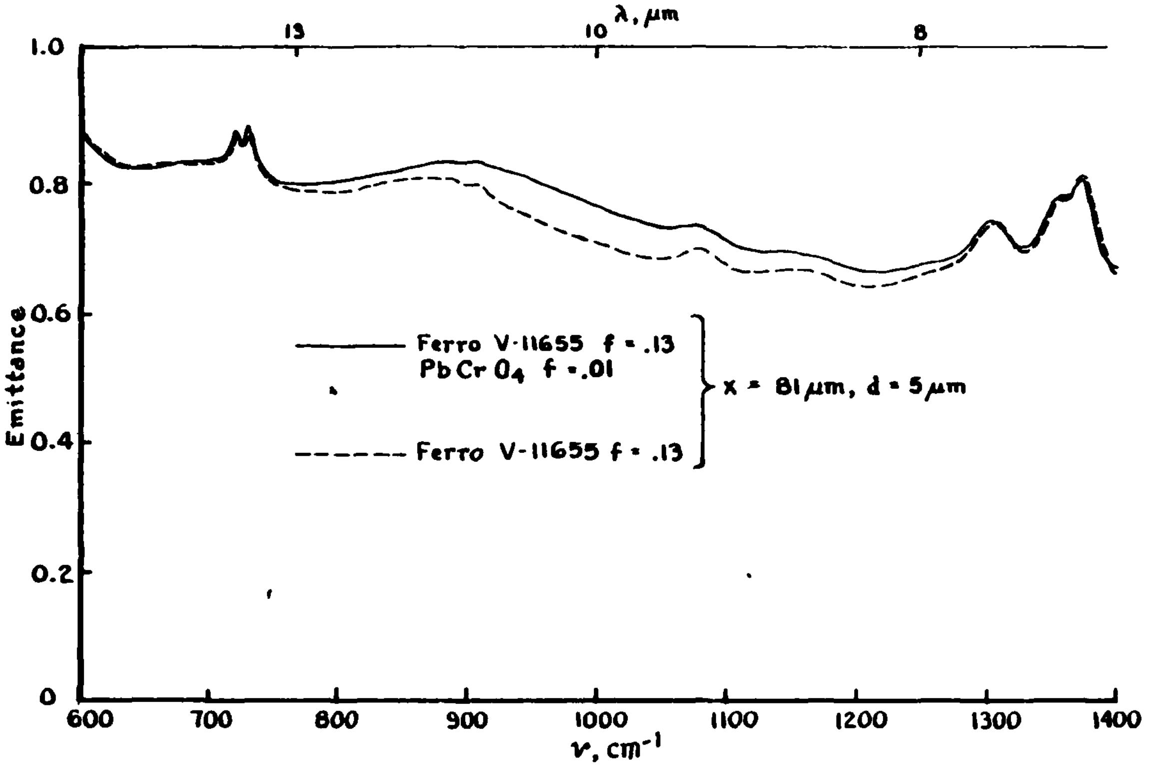
Figure 14



PARTICLE SIZE EFFECT ON PREDICTED SPECTRA OF FERRO V-11655 IN POLYETHYLENE
Figure 15

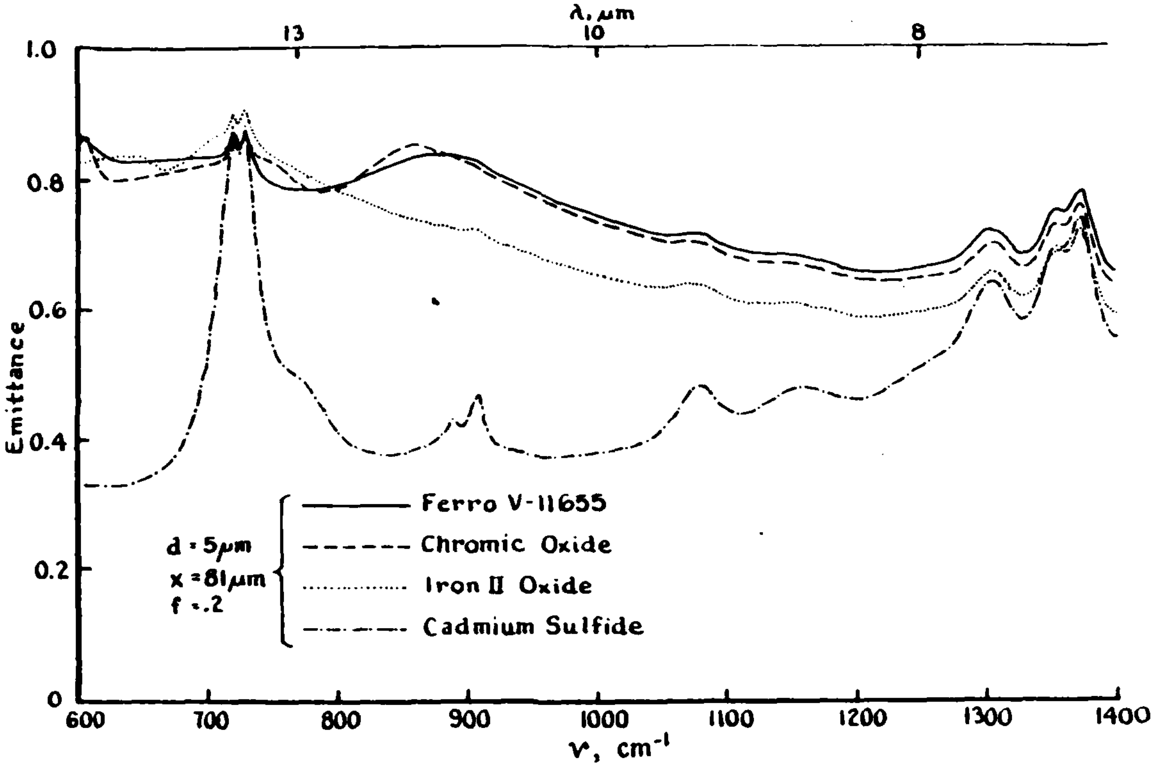
theoretical simulation, while not showing major effects for these particular sizes, is the kind of simulation that would enable one to pick the optimum particle size for the pigment. As the forest green paint contains other ingredients, principally chrome yellow, a simulation was run with a small amount of chrome yellow incorporated into the model in order to establish whether this pigment will cause problems. The results are shown in Figure 16 where it is seen that even a 1% by volume addition of chrome yellow will further increase the emittance of the paint. Thus it is clear that we need to obtain a better yellow pigment than chrome yellow.

As the performance of the Ferro green pigment has appeared to us to be unsatisfactory in the thermal infrared region, we examined a possible substitute - chromium oxide, using literature values[12] of the optical constants. Figure 17 shows the predicted emittance spectrum of a 20% by volume mixture of chromium oxide in polyethylene. The results are very closely similar to those for the Ferro pigment which are included on the same figure with the same other parameters. A similar run for Fe_2O_3, which is sometimes used as a yellow or red pigment[16] is also shown in the same figure. It is apparently somewhat better although not an ideal candidate as a pigment in this spectral region. Cadmium sulfide on the other hand shows a distinct improvement over any of these other pigments as can be seen from the figure. Cadmium sulfide is sometimes used as a yellow pigment[16] and owes its thermal infrared success, at least in our theoretical simulations, to the fact that its absorption bands are at much greater wavelengths than any of the other pigments thus far tested. If cadmium sulfide indeed could be shown to have this kind of performance and other pigments of the same type but differing colors could be found, the possibility of producing a very low emittance paint or coating is very good. In fact, as shown in Figure 18 addition of cadmium sulfide to the Ferro green pigment has some success in lowering the emittance of the green coating owing to the additional scattering of this high index infrared transparent material. A further increase in the cadmium sulfide concentration can still lower the



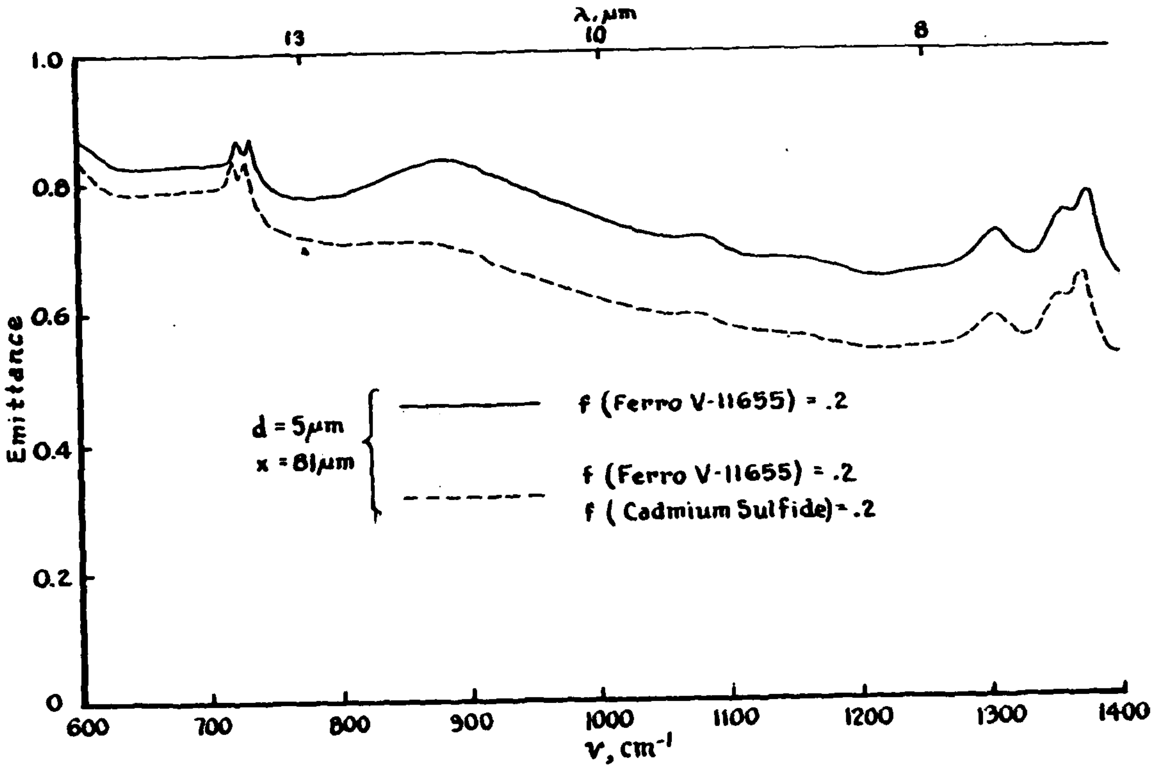
COMPUTER SIMULATION: EFFECTS OF CHROME YELLOW ON COATINGS

Figure 16



COMPUTER SIMULATIONS OF VARIOUS PIGMENTS IN POLYETHYLENE

Figure 17



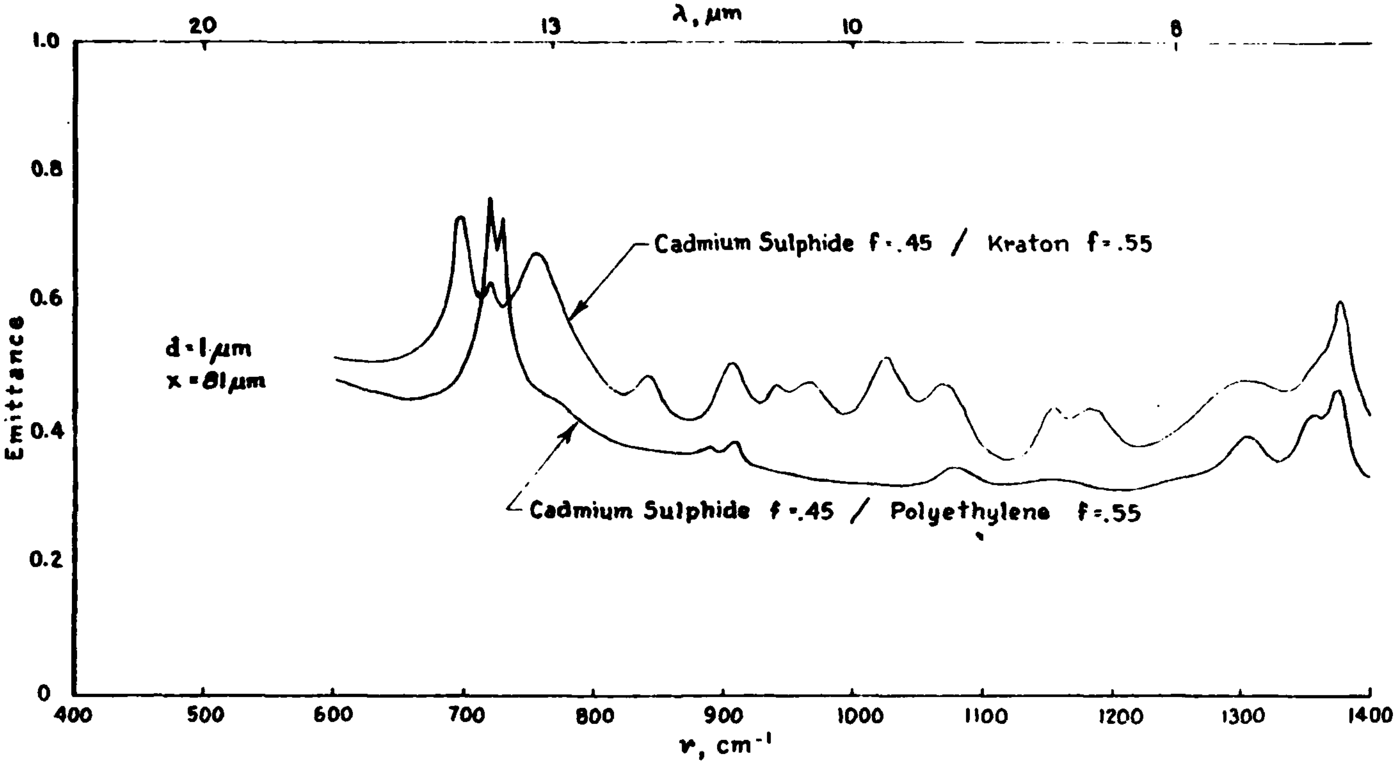
COMPUTER SIMULATION: EFFECT OF CADMIUM SULFIDE ON GREEN COATING

Figure 18

emittance of a yellow paint or coating as shown in Figure 19. In fact, it is successful even in the Kraton binder as can be seen, though of course the polyethylene binder is still to be preferred. As before the simulation near 720 cm^{-1} is dubious owing to fitting problems near the large peak at that frequency.

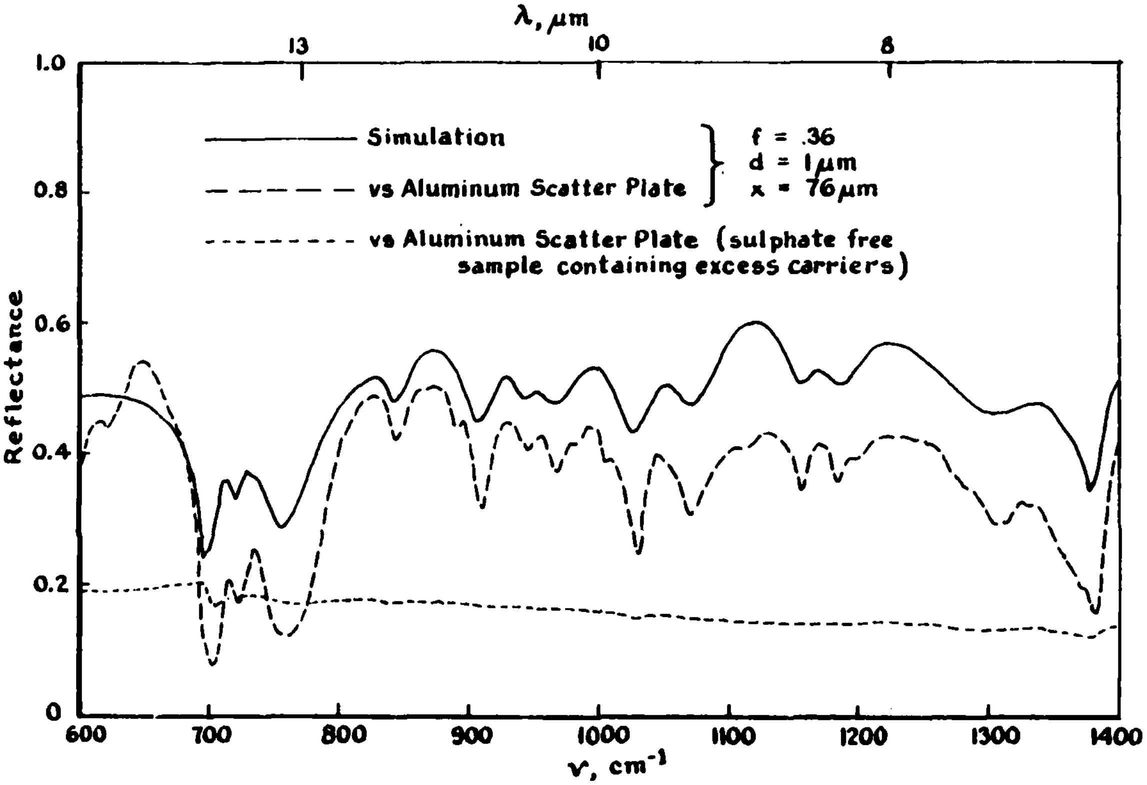
Some experiments were carried out to test the cadmium sulfide paint (Kraton binder) predicted by our theoretical simulations to be an excellent choice for one component of any future camouflage paint system. The results indicate that the cadmium sulfide pigment used for such work must be carefully specified. The sample obtained for our first experiments contain some sulfate which contributed to absorption in the thermal infrared region. When this material was washed out of the pigment and the experiment repeated only a small improvement in the paint characteristics could be noted. Discussion with other members of our staff led us to believe that the problem relates to the "purity" of the cadmium sulfide in that any additional cadmium present (lack of stoichiometry on the n type side) or defects created in the milling operation could provide free electrons that would increase the absorption of pigment far beyond what would be expected from its lattice vibrations.

To eliminate excess charge carriers we annealed some of the sulphate free cadmium sulfide in a sulphur atmosphere at 800°C in a quartz ampoule. The resulting product contained some large pieces of sintered material which were removed. The remainder was ultrasonically dispersed in a solution of Kraton in toluene and a new sample prepared from the product. This sample showed considerably enhanced reflectance using the Digilab FTS instrument with no evidence of free electron absorption. The Kraton features can now be clearly seen and the experimental data closely resemble the theoretical simulation (Fig. 20), although the reflectance spectrum is only qualitative as it was run against a scatter plate standard of uncertain absolute reflectance. Also included in Fig. 20 is the reflectance of a similar sample of the



COMPUTER SIMULATIONS: CADMIUM SULPHIDE COATINGS

Figure 19



COMPARISON OF CdS/KRATON PAINTS WITH SIMULATION

Figure 20

sulphate free cadmium sulphide paint, run against the same scatter plate. The latter sample showed a relatively flat emittance of approximately 0.95 when run in our emission apparatus. Unfortunately that apparatus is presently disassembled for modification so we are unable to run the improved sample.

The enhanced reflectance of the sulphur-annealed-pigment paint (reduced emittance) and its similarity to the simulated spectrum indicate that such a paint would serve as an improved yellow thermal camouflage material. Other colored pigments need to be developed to be mixed with the cadmium sulfide pigment to provide the basis for replacements for the eleven camouflage paints.

VI - Summary and Recommendations

A. Results

The principal results of the work described in this report are:

1) the theory of reflectance or emittance of particulate materials has been successfully modified so as to apply to paints and coatings of military interest.

2) The theory so modified is a useful tool that can predict the emittance or reflectance of proposed new coating systems, providing only that optical constants for the components are available.

3) Methods have been developed to derive optical constants for materials of interest for future paint or coating systems.

4) The insight gained from examination of the properties of the present Army camouflage paints and a knowledge of the physics of the

absorption and scattering of pigmented systems suggests ways that significant improvements can be made in tailoring the thermal emittance of paints or coatings. Such improvements should materially assist in reduction of the thermal signatures, which could be used by an adversary to locate and destroy military hardware.

5) Such improvements in the thermal infrared properties of paints and coatings may be made without deleteriously affecting the properties of those same paints or coatings in the visible region.

The first and most necessary requirement for improved paints and coatings in the thermal infrared region is the formulation of a suitable binder system that can serve to hold the various pigments selected, and at the same time is sufficiently transparent in the infrared region so as not to be the source of thermal emission itself. The present work has indicated that the Kraton system has the required thermal infrared properties as well as visual properties to provide the binder for new paint. Its physical properties will have to be further examined to establish the practicality of this material. Furthermore, should there be applications for coatings applied by different technologies than common in the paint industry or stand-alone type materials that may serve as radiation shields, polyethylene would be the binder of choice.

The present pigments being used in Army camouflage paints, specifically in forest green, are inadequate for thermal region camouflage.A search for improved pigments has been begun. These pigments will have to provide the camouflage colors desired for military systems but have their principal absorption bands located well outside the regions of atmospheric transparency so as to provide scattering but minimally absorbing characteristics.

B. Suggestions for Further Work

In order to provide a new and improved set of camouflage colors for military hardware, we suggest the following tasks be undertaken:

1) Pigmented Kraton and polyethylene systems both be explored with respect to such properties as abrasion resistance, weathering, application methods, adhesion, decontamination problems, and cost.

2) The search for new pigments be intensified so that the camouflage colors may be prepared by suitable mixtures of non-thermally emitting materials. This search would be aided by use of the already developed computer model so as to reduce the number of experimental measurements required.

3) The optical constants of likely candidates be obtained to facilitate the above task.

4) Experimental measurements be made throughout the spectral regions of interest (i.e. visible, near infrared and infrared) to confirm the predicted behavior of suggested paints or coatings.

C. Participating Scientific Personnel (includingContract DAAG-29-77-C-0011)

J.R. Aronson, A.G. Emslie, C.F. Grain, L.W. Guilmette, F. L. Johnston, E.V. Miseo, P.B. Monaghan, F.E. Ruccia, J.L. Rudolf, K.R. Sidman, I. Simon, C.R. Smallman, E.M. Smith, P.F. Strong and P.C. von Thuna

D. List of Publications (including Contract DAAG-29-77-C-0011)

"Infrared Emittance of Fibrous Materials," J.R. Aronson, A.G. Emslie, F.E. Ruccia, C.R. Smallman, E.M. Smith and P.F. Strong, Appl. Opt. 18, 2622 (1979)

"Modeling the Infrared Emittance of Paints," Final Report to MERADCOM on a related Contract (DAAK70-79-D-0036, Task Order No. 0008), J.R. Aronson and Alfred G. Emslie, Oct 1980

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