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A BONDING MATERIAL FOR OPTICALLY IMMERSING INFRARED DETECTORS FROM 2 TO 14 MICRO-METERS

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ABSTRACT

The visible and infrared transmitting properties of a specific epoxy resin are analyzed and shown to be suitable for bonding infrared detectors, operating in the 2-14 μm spectral region, to an optically transmitting substrate for immersed applications; additionally, this resin permits preliminary system alignment using visible radiation. The resin also has desirable physical properties for such bonding applications.

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SUMMARY

A suitable bonding material for optically immersing infrared detectors has been found for the 2 to 14 micro-meter (μm) wavelength region, which contains several (8 to 14, 4.4 to 5, 2.9 to 4.2, and 1.9 to 2.5 μm) atmospheric windows of importance for such applications as Earth resources and other terrestrial mapping, optical communications from Earth to satellites and other bodies, horizon sensors, and ground-based infrared astronomy. This material cures to films having flexural and compressive strengths in excess of 10^4 lb/in.^{2}, high moduli and heat distortion temperatures, and good visible transmittance to assist in detector and optical system alignment. Its infrared transmission properties are measured and analyzed herein in combination with two substrate materials which transmit radiation well in the spectral range of interest.

INTRODUCTION

Araldite 6010 is the trade name for an unmodified, light amber-colored liquid epoxy resin which transmits visible radiation well, cures at room temperature to a film having high chemical and electrical resistance, and adheres very well to metals, ceramics, semiconductors, and other materials. Because of these properties, this resin appears to be well suited to securing optical radiation detectors to their substrates, after which the devices can be processed, i.e., lapped and mechanically polished, chemically etched to a desired thinness, have leads attached, and be passivated. The substrate is essential in prevention of the thin semiconductor wafer from breaking during processing (typical intrinsic detector thicknesses are of the order of 1 mil.) For a number of applications, it is desirable to "immerse" the detector optically; that is, to transmit signal radiation through the substrate and cement into the detector. This has advantages such as passivating (encapsulating) the radiation detecting surface, reducing reflective radiation losses, or (in the case of a lens) increasing detectivity by increasing the effective detector sensitive area (and thus the signal) without increasing detector noise. The infrared transmittance of Araldite 6010 epoxy films is studied here in the 2 to 14 μm wavelength spectral region.

SELECTION OF EXPERIMENTAL MATERIALS

If the detector is to be optically immersed in a given case, then it is necessary that both the substrate and cementing material be highly transparent to radiation of wavelengths at which the detector is sensitive. Thus the incident radiation is nearly completely absorbed by the detector element and contributes to an electrical signal rather than becoming lost in its passage through the intervening material.

Many solid materials are known which transmit infrared radiation very well out to (and, in some cases, beyond) 14-µm wavelength - the limit of high atmospheric transmittance. Among these are silicon, germanium, and selenium; barium, lead and sodium fluorides; cadmium sulfide and telluride; various arsenic-, iodine-, and selenium-containing infrared glasses; potassium, silver, thallium, and sodium chlorides; the KRS's; thallium and cesium bromides; and potassium and cesium iodides (ref. 1). In addition, Kodak hot-pressed polycrystalline powders, called "Irtrans" for InfraRed TRANsmitting, are useful. They are numbered 1 through 6, and are, respectively, magnesium fluoride, zinc sulfide, calcium fluoride, zinc selenide, magnesium oxide, and cadmium telluride. Their long-wavelength (10 percent for 0.080 inch thickness) transmission limits are, respectively, 9.2, 14.7, 11.5, 21.8, 9.4, and approximately 32 µm from number 1 through 6 (ref. 2).

Among the factors which must be considered in selecting a suitable detector substrate material are coefficient of thermal expansion (to match that of the detector), thermal conductivity (to transfer heat from detector to cryogen), moduli of elasticity and rupture, softening point, solubility, and chemical resistance. Radiation reflection losses are covered in the transmission measurement, and may be reduced by appropriate interfacing on one side and antireflection coating on the other. The Irtrans were selected for good physical and chemical properties, and the Irtran-2 (long-wavelength cutoff 14.7 µm) coefficient of thermal expansion is sufficiently close to that of a number of useful detector materials. The best transmitting material in the 7- to 14-µm region appears to be barium fluoride, useful in the experimental work to be described, but slightly soluble in water (ref. 3), of poor chemical resistance, and with an extremely high coefficient of thermal expansion; thus, it has definite limitations as an infrared window or as a detector substrate material.

Relative to the cementing material used to bond the detector to its substrate, certain properties are useful:

(1) Low vapor pressure,
(2) Good adhesion,
(3) Room temperature setting,
(4) Transparent in the visible region,
(5) Good chemical stability and insolubility,
(6) Transparent to radiation in the IR region of interest.

Low vapor pressure is a requirement to avoid outgassing and vacuum deterioration in the evacuated dewar in which the detector is stored. This prevents condensation on the detector and window during cryogenic operation. Gold lead wires and pure indium and indalloy solders, typical for IR detectors, fulfill this requirement (ref. 4). Most common substrate materials also meet this criterion (ref. 5).

Good adhesion is a requirement because it is necessary that the detector remain firmly in place under all conditions, including large temperature changes when the detector element is cooled to a cryogenic (operating) temperature.

It is desirable that the cement harden to ultimate physical strength ("set") at room temperature. Some detectors are sensitive to elevated temperatures (e.g., HgCdTe tends to decompose because of the HgTe content).

Transparency in the visible region for both cement and substrate would permit optical system alignment of an immersed detector visually prior to final IR adjustment. It also assists the fabricator to eliminate bubbles from the cement film for maximum adhesion and thermal conductivity.

High chemical stability is essential to prevent undesirable side reactions with various detector etchants, and the cement must be essentially insoluble in typical rinsing solvents (water, alcohol, acetone, chlorinated hydrocarbons). This also maintains film integrity and prevents later outgassing during detector storage in an evacuated dewar.

If an immersed detector is to receive maximum signal radiation, the substrate and cement must be as highly transmitting of radiation in the sensitive spectral region of the detector as possible. This varies according to the detector material.

Araldite 6010 epoxy resin with amine hardener HN 951 meets all the desirable properties discussed above (ref. 6); in addition, it has high electrical resistance, tensile, compressive, and flexural strengths of 9,000, 23,000, and 17,000 lb/in.^{2}, respectively, 0.004 inch/inch shrinkage during cure; and low water absorption (ref. 7). It was selected as the test material to determine transmittance at various infrared wavelengths of particular interest in IR detector research and development. Both barium fluoride and Irtran-2 were selected to be used with the epoxy because of their high and known IR transmittance out to 14-μm wavelength. Figures 1 and 2 show the typical transmittances (refs. 1 and 2, respectively, recalculated to NASA sample thicknesses) versus actual experimental measurements.

ANALYSIS OF EXPERIMENTAL WORK

Epoxy with Barium Fluoride

Two optically flat and polished samples of barium fluoride were individually measured for infrared transmittance. The transmittance measurements were identical for both pieces within experimental error and are shown in Figure 1. Each piece was 3 mm (0.12 inch) thick. The two pieces were then cemented together with Araldite 6010 epoxy resin and cured with 13 parts (per 100 parts of resin) of hardener HN 951. Care was taken to remove all air bubbles and to make the epoxy layer thin. The transmittance of the cemented assembly was measured and is shown in Table I.

The expressions for reflectance, absorptance, and transmittance for a single flat piece of material are well known (for example, see ref. 7). For multiple layers, the expressions become more complicated. The general expression for the total transmittance of three layers in series (as, for example, a substrate, epoxy bonding layer, and semiconductor), allowing for multiple internal reflections, is:

TABLE I

TRANSMITTANCE OF CEMENTED BARIUM FLUORIDE ASSEMBLY

Wavelength μm	External Transmittance %
8	17
9	68
10	66
11	58
12	20
13	16.7

$$\tau_t = \left[\frac{(1-\rho_{as})(1-\rho_{sc}) \exp(-\alpha_s d_s)}{1-\rho_{as}\rho_{sc} \exp(-2\alpha_s d_s)}\right] \cdot \left[\frac{(1-\rho_{sc})(1-\rho_{cb} \exp(-\alpha_c d_c)}{1-\rho_{sc}\rho_{cb} \exp(-2\alpha_c d_c)}\right] \cdot \left[\frac{(1-\rho_{cb})(1-\rho_{ba}) \exp(-\alpha_b d_b)}{1-\rho_{cb}\rho_{ba} \exp(-2\alpha_b d_b)}\right] \tag{1}$$

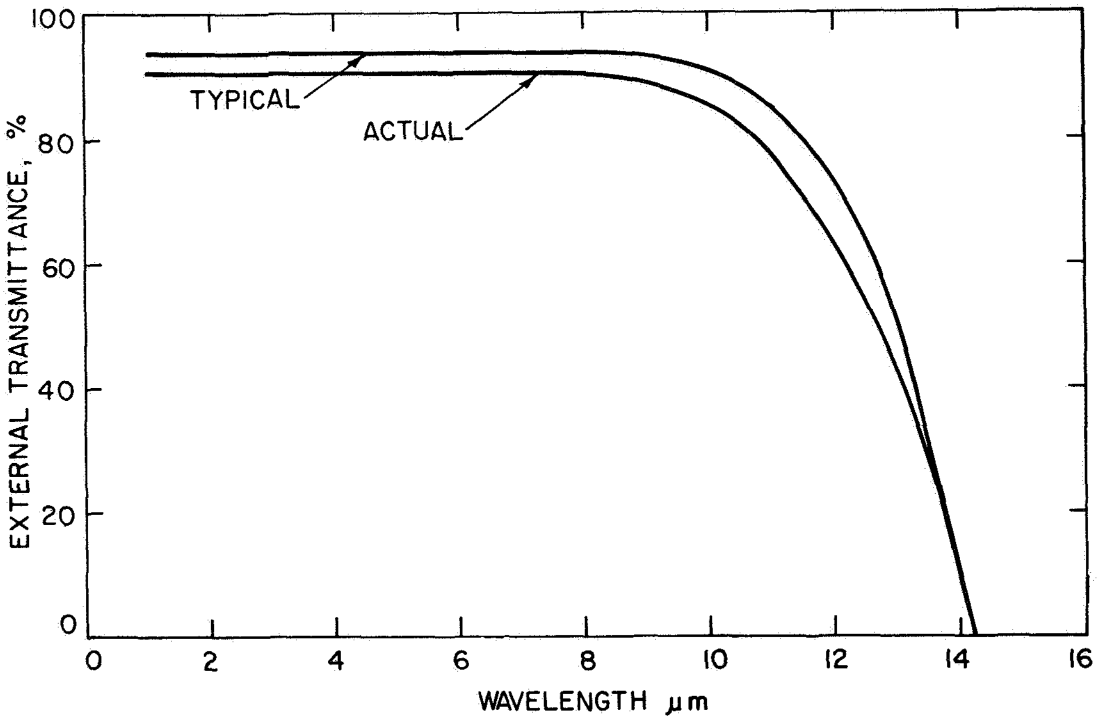


Figure 1. - Typical and actual transmittances of barium fluoride (External transmittance of 3-mm thick sample)

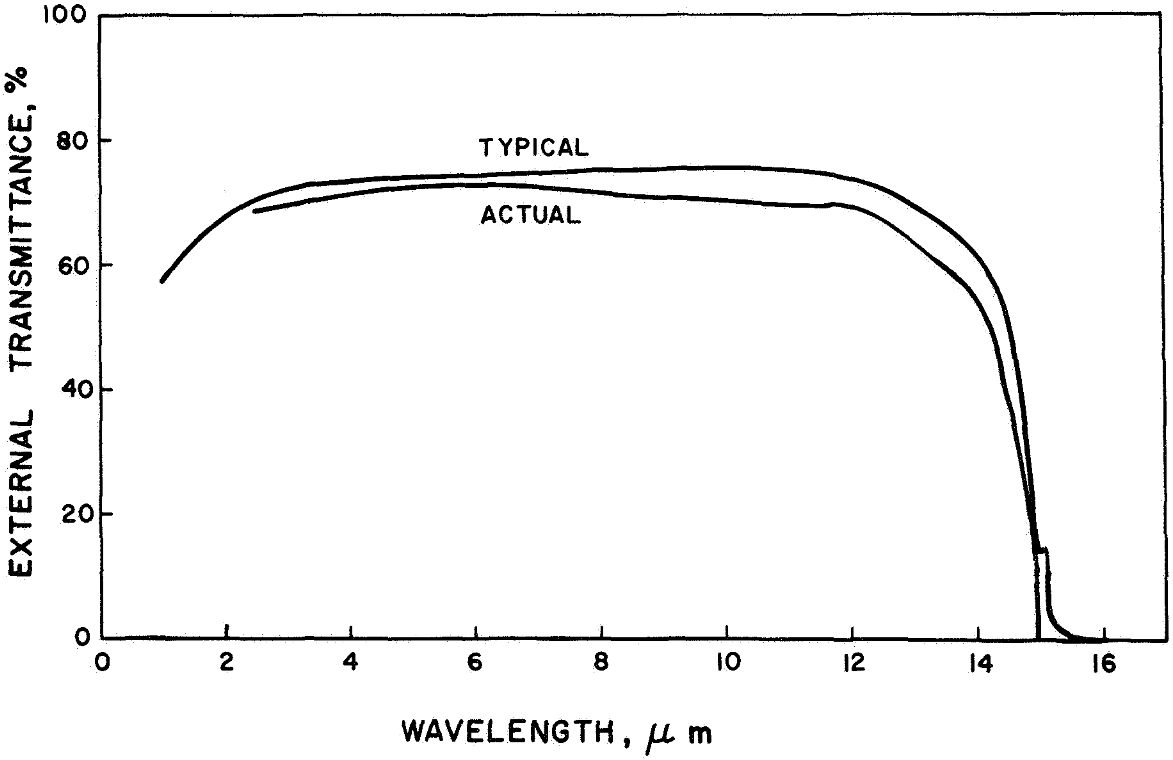


Figure 2. - Typical and actual transmittances of Irtran-2 (External transmittance of 1-mm thick sample)

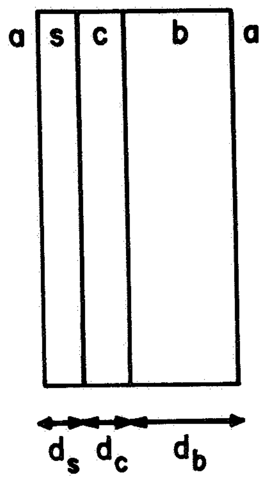
where

τ_t = total transmittance (allowing for multiple reflections)

ρ = reflectivity

α = absorption coefficient

d = distance through (thickness of) the layers, as in sketch at right



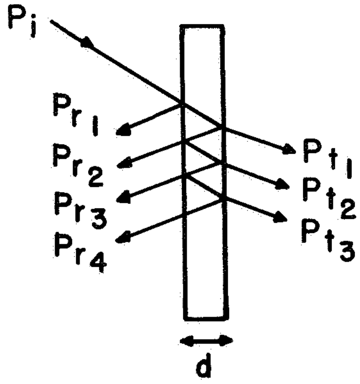
The subscripts a, s, c, and b refer, respectively, to air, semiconductor, cement, and substrate.

For radiation of photon energy larger than the forbidden bandgap of a direct gap semiconductor, the absorption coefficient is often very high (~10^4 to 10^5 cm^{-1}) and thus very little radiation will penetrate the assemblage shown. However, in the present work, sandwiches of substrate and cement which transmitted appreciable (and easily measurable) radiant power were fabricated. For this case, Eq. (1) also holds.

For this simpler case of a single substrate, the incident, reflected, and transmitted rays can be shown without confusion, and are diagrammed below. Equation (1) simplifies for this case to

$$\tau_t = \frac{\sum_{n=1}^{\infty} P_{t_n}}{P_i}$$

$$= \frac{(1-\rho)^2 \exp(-\alpha d)}{1-\rho^2 \exp(-2\alpha d)} \quad (2)$$



where P_t and P_i are transmitted and incident radiant powers, respectively, and ρ the reflectivity of the substrate surface (air-substrate interface). For two substrates of equal thickness with a short air path between, the transmittance may be approximately found by squaring the right-hand side of Eq. (2):

$$\tau_t = \frac{(1-\rho)^4 \exp(-2\alpha d)}{1 - 2\rho^2 \exp(-2\alpha d) + \rho^4 \exp(-4\alpha d)} \qquad (3)$$

for a spectral range over which the optical absorption coefficient of the material may be considered constant.

It should be mentioned that the reflectivity of an interface is the same for either direction of travel of the radiation. This arises from the fact that

$$\rho_{cb} = \frac{\left(N_c - N_b\right)^2 + K^2}{\left(N_c + N_b\right)^2 + K^2} \quad .$$

For transmitting media, the extinction coefficient K is generally negligible, and

$$\rho_{cb} = \left|\frac{(N_c - N_b)}{(N_c + N_b)}\right|^2 \equiv \rho_{bc} \quad . \qquad (4)$$

When, for the moment, radiation absorption for the two barium fluoride (BaF_2) windows is neglected, the exponential terms may be dropped from the transmittance equations and written:

$$\frac{\tau_t \text{ (air film between)}}{\tau_t \text{ (cemented with epoxy)}} = \frac{\left[\dfrac{\left(1-\rho_{ab}\right)^4}{\left(1-\rho_{ab}{}^2\right)^2}\right]}{\left[\dfrac{\left(1-\rho_{ab}\right)^2\left(1-\rho_{bc}\right)^2}{\left(1-\rho_{ab}\rho_{bc}\right)^2}\right]}$$

$$= \frac{\left(1-\rho_{ab}\right)^2\left(1-\rho_{ab}\rho_{bc}\right)^2}{\left(1-\rho_{bc}\right)^2\left(1-\rho_{ab}{}^2\right)^2} \qquad (5)$$

With the values of $N_a = 1$ (air), $N_b = 1.421$ at 9.7 μm and 1.414 at 11.0 μm, and $N_c = 1.573$ (manufacturer's unpublished data), at 10 μm wavelength, from Eq. (4), $\rho_{ab} = 0.0301$ and $\rho_{bc} = 0.00251$. Thus $\tau_t(a)/\tau_t(c) = 0.950$ from Eq. (5). This result shows that the predicted external transmittance of the cemented windows is higher than that of the windows with a thin film of air between them, and the reason is that refractive indix matching at the epoxy-BaF_2 interface reduces reflection losses below those of BaF_2 in air. The experimental ratio (from Figure 1 and Table I) is:

$$\frac{\tau_t(a)}{\tau_t(c)} = \frac{0.739}{0.66} = 1.12 ,$$

indicating that the epoxy actually does absorb some radiation, an amount which will now be calculated.

The two-surface reflection loss for BaF_2 is given as 7.7 percent at 0.6 μm (ref. 1, p. 34) and the transmittance curve indicates that this value is essentially constant out to a 10-μm wavelength. It is probably safe to consider it constant throughout the spectral region of interest, since absorptance rather than increased reflectance causes the drop in the transmittance curve. The refractive index data of reference 1 show this. Since $I = I_o \exp(-\alpha d)$, when absorption loss only (internal transmittance) is considered, calculation for the BaF_2 may be performed by means of

$$\frac{I}{I_o} = \exp(-0.3\alpha_b) .$$

TABLE II

ABSORPTION COEFFICIENT, α_b
OF BARIUM FLUORIDE

Wavelength μm	α_b, cm^{-1}
8	0.0469
10	0.241
13	2.63

Values of α from the experimental (I/I_o) are due only to absorption losses as shown in Table II. Now, when corrections for absorption are made, the absorption coefficient of the epoxy cement, α_c may be calculated, (at 10 μm):

$$\frac{\tau_t(a)}{\tau_t(c)} = \frac{\left[\dfrac{(1-\rho_{ab})^2 \exp\left(-\alpha_b d_b\right)}{1-\rho_{ab}^2 \exp\left(-2\alpha_b d_b\right)}\right]^2}{\left[\dfrac{(1-\rho_{ab})(1-\rho_{bc}) \exp\left(-\alpha_b d_b\right)}{1-\rho_{ab}\rho_{bc} \exp\left(-2\alpha_b d_b\right)}\right]\left[\dfrac{(1-\rho_{bc})^2 \exp\left(-\alpha_c d_c\right)}{1-\rho_{bc}^2 \exp\left(-2\alpha_c d_c\right)}\right]\left[\dfrac{(1-\rho_{bc})(1-\rho_{ab}) \exp\left(-\alpha_b d_b\right)}{1-\rho_{bc}\rho_{ab} \exp\left(-2\alpha_b d_b\right)}\right]}$$

$$= \frac{(1-\rho_{ab})^2 \left[1-\rho_{ab}\rho_{bc} \exp\left(-2\alpha_b d_b\right)\right]^2 \left[1-\rho_{bc}^2 \exp\left(-2\alpha_c d_c\right)\right]}{(1-\rho_{bc})^4 \left[\exp\left(-\alpha_c d_c\right)\right] \left[1-\rho_{ab}^2 \exp\left(-2\alpha_b d_b\right)\right]^2} = 1.12 \qquad (6)$$

Solving Eq. (6) by trial, measuring a 1-mil thickness of epoxy cement [d_c = 0.001 (2.54) cm] yields the absorption coefficient for the Araldite 6010 (α_c = 62 cm^{-1}). This means that a (typical) 1-mil thickness of Araldite 6010 would absorb about 14.8 percent of incident 10-μm radiation.

Epoxy with Irtran-2 (Zinc Sulfide)

An optically flat and polished window of Kodak Irtran-2 (hot-pressed polycrystalline zinc sulfide, 1-mm thick) was measured for infrared transmittance. It was then coated with a 1-mil-thick layer of Araldite 6010 epoxy cured at room temperature with 13 parts of hardener HN 951 per 100 parts resin. The measured transmittance of the Irtran-2 is shown in Figure 2. The transmittance of window plus epoxy is shown in Figure 3, and figures at selected wavelength increments are as follows:

TABLE III

ABSORBANCE OF IRTRAN-2 WITH ARALDITE 6010 EPOXY FILM

Wavelength λ, μm	Absorbance = log (1/τ)	External τ
2.5*	0.144	71.7
4	0.159	69.3
6	0.143	71.9
8	1.23	5.89
8.6	0.29	51.3
10	0.296	50.6
10.6**	0.255	55.6
11	0.265	54.3
12.5	0.33	46.8
14	0.39	51.3
15***	1.3	5.01
16	~10	10^{-8}

*Spectrophotometer minimum
**CO_2 laser
***Long wavelength cutoff of Irtran-2

The absorption coefficient of the epoxy comment, α_c, will now be calculated. The nomenclature will be the same as in the previous section except that subscript I will refer to Irtran-2. The two-surface reflection loss for Irtran-2 is approximately 20 percent between 2.5 and 12 μm wavelength:

$$\frac{I}{I_o} = \exp\ (-0.1\alpha_I)\ .$$

Between 2.5 and 12 μm, $\alpha_I = \ln 0.9/-0.1 = 1.05\ \mathrm{cm}^{-1}$. In this interval, an equation for calculating α_c may be stated:

$$\tau_t\ (\text{Irtran, I, plus cement, c}) = \frac{P_t}{P_i}$$

$$= \left[\frac{\left(1 - \rho_{aI}\right)\left(1 - \rho_{Ic}\right)\exp\ \left(-\alpha_I d_I\right)}{\left[1 - \rho_{aI}\rho_{Ic}\exp\ \left(-2\alpha_I d_I\right)\right]}\right]$$

$$\cdot\left[\frac{\left(1 - \rho_{Ic}\right)\left(1 - \rho_{ca}\right)\exp\ \left(-\alpha_c d_c\right)}{\left[1 - \rho_{Ic}\rho_{ca}\exp\ \left(-2\alpha_c d_c\right)\right]}\right]$$

$$= \frac{\left(1 - \rho_{aI}\right)\left(1 - \rho_{Ic}\right)^2\left(1 - \rho_{ca}\right)\left[\exp\ \left(-\alpha_I d_I - \alpha_c d_c\right)\right]}{\left[1 - \rho_{aI}\rho_{Ic}\exp\ \left(-2\alpha_I d_I\right)\right]\left[1 - \rho_{Ic}\rho_{ca}\exp\ \left(-2\alpha_c d_c\right)\right]}\ . \tag{7}$$

$\rho_{aI} = 0.141$, $\rho_{Ic} = 0.0277$, and $\rho_{ca} = 0.0496$ from Eq. (4). Substituting these numbers, at 10.6 μm, yields:

$$\tau_t = 0.556$$

$$= \frac{(1 - 0.141)(1 - 0.0277)^2(1 - 0.0496)[\exp -1.05(0.1) - 0.00254\alpha_c]}{\{1 - 0.141(0.0277)[\exp -(2)(1.05)(0.1)]\}\{1 - 0.0277(0.0496)[\exp -2(0.00254\alpha_c]\}} \tag{8}$$

which may be immediately simplified to

$$\frac{\exp(-0.00254\alpha_c)}{1 - 0.001375 \exp(-0.00508\alpha_c)} = 0.772$$

Solving by trial, $\alpha_c = 101\ \text{cm}^{-1}$, which indicates that a 1-mil thickness of Araldite 6010 transmits about 77 percent of the incoming 10.6-μm radiation. It may be seen from Figure 3 that the Araldite transmittance is nearly at a peak at 10.6 μm; thus it is a good bonding material for an immersed CO_2 laser detector.

An additional coating of Araldite 6010 was used to cement a second Irtran-2 window to the first. The absorbance data for the cemented doublet are shown in Figure 4, and indicate that although there is 10 percent external transmittance at 10.6 μm, there are a number of spectral regions of essentially zero transmittance. Clearly, for high radiation transmission, the epoxy should be applied as a single thin coat and kept clean. Necessary handling of the initial coated window during measurements may have reduced its infrared transparency.

CONCLUSIONS

Araldite 6010 epoxy resin, cured with 13 parts per 100 by weight of hardener HN 951, is a promising bonding material for immersed infrared detectors in the 2- to 14-μm wavelength region. It is also transparent to visible radiation for device and optical component alignment purposes.

Although absorption regions occur at intervals over the above spectral range, they generally are not at critical wavelengths. With reference to Figure 3, there is relatively heavy absorbance at 3.0, 3.4, 6.2 to 8.5, 9.7, and 12.2 μm. Similar absorption regions are probably inevitable with other organic materials.

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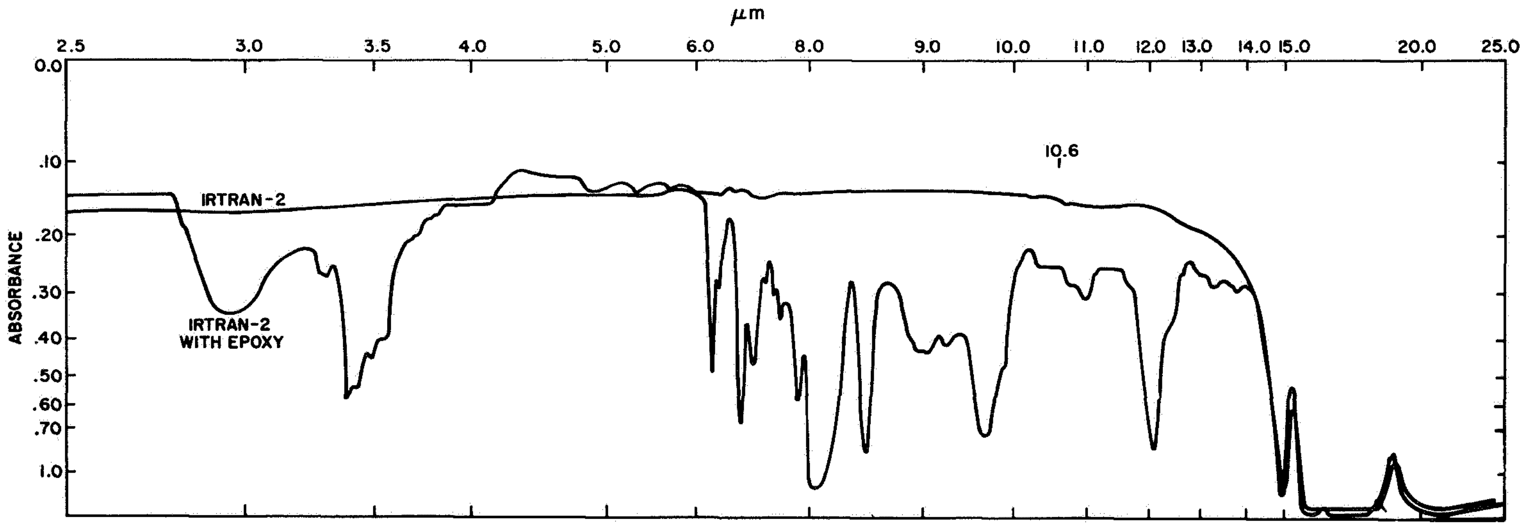

Figure 3. - Absorbance of Irtran-2 and Araldite 6010

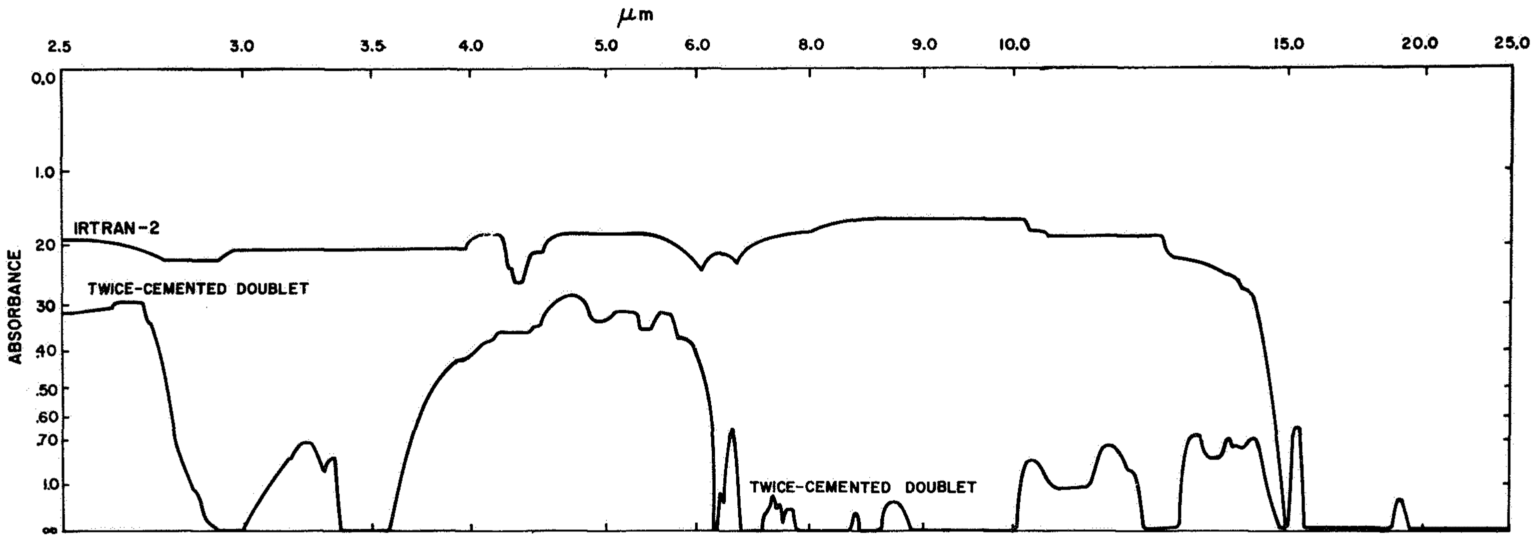

Figure 4. - Absorbance of Irtran-2 and cemented doublet

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