

ACKNOWLEDGEMENTS

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COLLOIDAL CARBON AND SILICA :
being patient with me and for undertaking the unenviable task of
THEIR USE IN SOLAR ENERGY
supervising me.

I suppose I must also thank some of the student regulars (Ian Gentle,
Jenny Green, David Everett, Bruce New York, Gary Dennis, John Feeney etc.)
because if I didn't they may not thank me when they write their theses.

Much gratitude also goes to the Service room and General Chemistry
Being a thesis submitted to the
staff for making me feel at home, although I wish the former would get my
University of Sydney
name right.

for admission to the degree

Master of Science

I also would like to express my appreciation for the work done by the
Electron Microscope Unit, especially Ian Kaplin, for without them I would
never have experienced the JOEL 100CX.

A big "thank you" goes to the department of Applied Physics for funding
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actually laughed at them.

By

Leaving the best till last, I warmly express my affection for my
Raimonds Maris Vegners
beloved Susan Stellino who has not only given me much happiness but helped
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February 1985

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The aims of this thesis are to optimise the use of colloidal carbon and silica in photothermal solar selective surface coatings and colloidal used and researched are solar ponds, aerogenerators (windmills) and collectors for photothermal and photovoltaic conversions.

(i) Photothermal solar selective coatings.

1.1 PHOTOVOLTAIC

Using an effective medium theory (Maxwell Garnett equation) and the experimental determination of the conversion efficiency, the optimum volume fraction and film thickness of the colloidal carbon and silica coatings can be determined. The temperature stability of these coatings will also be discussed.

charges which can then be separated to develop a voltage and current.

Semiconductors are the most suitable materials for photovoltaic solar cells

(ii) Antireflection coatings.

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1982, 10% conversion of solar energy was reported /4/. Recently much interest has been shown in amorphous silicon arrays /5/ where theoretical

Chemical bath dipping procedures will be used in this thesis as a means solar energy conversions of up to 26% are predicted.

of applying the coatings. This is seen as an economically attractive method

in fabricating these films.

1.2 PHOTOTHERMAL (see section 2)

Photothermal energy conversion involves the heating of a medium by the absorption of solar radiation. The heated medium could then be used for heating, air conditioning or for running generators to produce electricity.

To maximise the efficiency of the absorbing surface, the surface must stop black body radiation. This can be achieved by surfaces that selectively absorb energy in the visible spectral range and reflect infrared radiation.

SECTION 1 SOLAR ENERGY

Among the many types of solar energy devices /1,2/ the most commonly used and researched are solar ponds, aerogenerators (windmills) and collectors for photothermal and photovoltaic conversions.

1.1 PHOTOVOLTAIC

The photovoltaic effect involves the conversion of solar radiation into electrical power. This is achieved by the absorption of photons (causing electronic excitations) to create equal numbers of positive and negative charges which can then be separated to develop a voltage and current. Semiconductors are the most suitable materials for photovoltaic solar cells in which electrostatic fields can be incorporated in order to separate the photogenerated electrons and holes.

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1.2 PHOTOTHERMAL (see section 2)

Photothermal energy conversion involves the heating of a medium by the absorption of solar radiation. The heated medium could then be used for heating, air conditioning or for running generators to produce electricity. To maximise the efficiency of the absorbing surface, the surface must stop black body radiation. This can be achieved by surfaces that selectively absorb energy in the visible spectral range and reflect infrared radiation.

1.3 ANTIREFLECTION COATINGS

INTRODUCTION TO PHOTOTHERMAL SURFACES

2.1 To reduce reflective losses incurred on the glass protective covers of solar collecting surfaces, antireflection coatings are required. Among many types of antireflection coatings (see section 6), colloidal silica coatings have the optical properties that make it a viable (cheap and efficient) prospect. Intensity can be represented by:

$$I = R + A + T \quad (2.1)$$

where I , R and T denote the intensities of the incident, reflected and transmitted light respectively, and A is the absorbed intensity.

To render a surface applicable for use in a solar collector the surface must absorb as much of the sun's energy obtained here on earth and transfer this energy to the medium that is to be heated. To maximize the absorption, the transmittance and reflectance must be minimized and this can be achieved by the collector design, antireflection coatings and surface roughening. High absorbance is not the only criterion for a good solar collector because radiative losses can be incurred from the surface at the high temperatures obtained by solar absorption. This radiative loss is known as black body radiation and to obtain efficient solar conversion this loss must be stopped.

The radiated power of black body radiation is related to the temperature of the body and is given by:

$$P = \sigma_e T^4 \quad (2.2)$$

where P is the total radiated power of a black body, σ_e is the thermal

SECTION 2

INTRODUCTION TO PHOTOTHERMAL SURFACES

2.1 SURFACE PROPERTIES

Light can either be absorbed by, transmitted through or reflected from a homogeneous surface. The relationship between absorption, transmittance and reflectance can be represented by:

$$I = R + A + T \quad (2.1)$$

where I, R and T denote the intensities of the incident, reflected and transmitted light respectively, and A is the absorbed intensity.

To render a surface applicable for use in a solar collector the surface must absorb as much of the sun's energy obtained here on earth and transfer this energy to the medium that is to be heated. To maximise the absorption, the transmittance and reflectance losses need to be minimised and this can be achieved from the collector design, antireflection coatings and surface roughening. High absorptance is not the only criterion for a good solar collector because radiative losses can be incurred from the surface at the high temperatures obtained by solar absorption. This radiative loss is known as black body radiation and to obtain efficient solar conversion this loss must be stopped.

The radiated power of black body radiation is related to the temperature of the body and is given by:

$$P = e_t \sigma T^4 \quad (2.2)$$

where P is the total radiated power of a black body, e_t is the thermal

emittance, T is the temperature of the body and σ is the Stefan-Boltzman constant ($5.6693 \times 10^{-8} \text{ W.m}^{-2}\text{.K}^{-4}$). To give an idea of how significant this radiative loss is, the power radiated by typical high performing solar collector (surface temperature of around 300°C) is 14 fold more than a body at room temperature.

According to Wien's Displacement Law on black body radiation the wavelength for the peak emission of energy is given by:

$$\lambda_{\text{max}}T = 2897.8 \text{ } \mu\text{m.K} \quad (2.3)$$

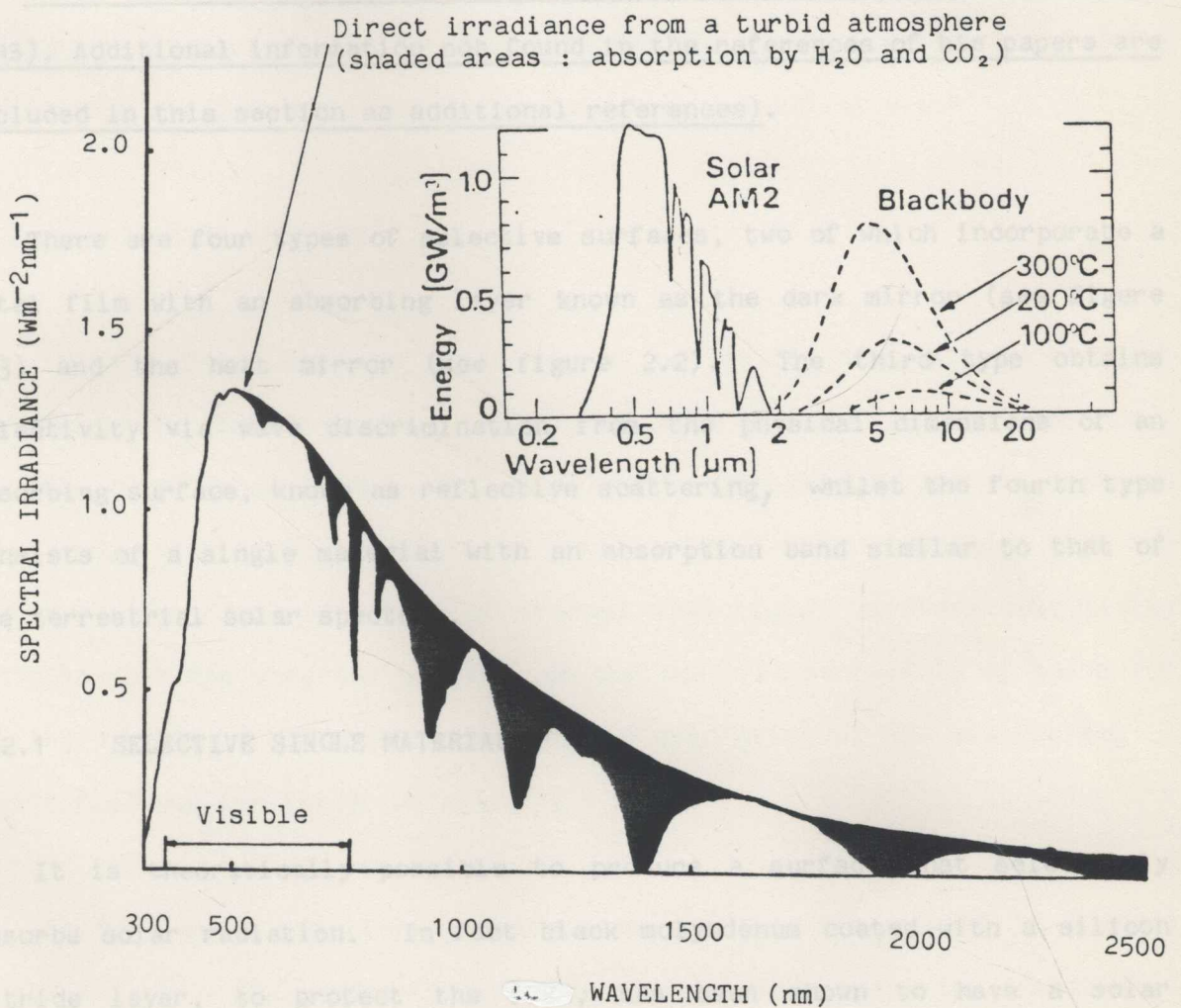
In relation to the spectral profile of black body radiation, 99% of the re-radiated power occurs at wavelengths longer than $0.4\lambda_{\text{max}}$ (see figure 2.1). For solar cell operating temperatures of around 300°C (which are the temperatures expected for evacuated cell set-ups, see section 2.3) 99% of the black body radiated energy has wavelengths of $2\mu\text{m}$ and longer, whilst for operating temperatures of around 150°C (which are the temperatures aimed for in this project) $0.4\lambda_{\text{max}}$ is approximately $2.7\mu\text{m}$ (see figure 2.1).

If one wishes to suppress this energy loss, the solar collecting surface must be a poor emitter of energy at wavelengths longer than $2\mu\text{m}$. A method of achieving this is to fabricate a film which selectively absorbs energy over the range of wavelengths incident on the earth's surface and acts as a good infrared reflector (i.e. poor emitter for the wavelengths of the black body radiation). This reflection effectively prevents the absorbed energy from being re-radiated out of the collector surface. One way of achieving this selectivity is to incorporate a metal film which is reflective to infrared radiation. Speaking qualitatively this means that as the metal reaches high temperatures (300°C in this case) the energy

would be transferred via lattice vibrations (i.e. conduction) to the surrounding medium - presumably water - but not lost from the system.

At this point it should be mentioned that although wavelengths longer than $2\mu\text{m}$ of the incident solar flux are reflected, this energy accounts for only 5% of the total solar radiation at the earth's surface [6]. The bulk of the energy obtained here on earth from the sun lies between $0.3\mu\text{m}$ and $2.5\mu\text{m}$ (see figure 2.1).

FIGURE 2.1 SOLAR SPECTRAL DISTRIBUTION CURVE



(AM2 = Clear weather)

The usual method of stating the performance of a solar selective surface is to quote the solar absorptance, a_s , and the thermal emittance, e_t . The solar absorptance is expressed as the fraction of energy absorbed compared to that of the incident solar flux (commonly approximated by tungsten light) and the thermal emittance is the fraction of the energy radiated compared to a black body at a temperature of 50°C. Typically a good selective surface will have $a_s > 0.90$ and $e_t \approx 0.05$.

2.2 TYPES OF SURFACES

(This section is mainly based on B.O. Seraphin's work (references 11-13). Additional information not found in the references of his papers are included in this section as additional references).

There are four types of selective surfaces, two of which incorporate a metal film with an absorbing layer known as the dark mirror (see figure 2.3) and the heat mirror (see figure 2.2). The third type obtains selectivity via wave discrimination from the physical dimensions of an absorbing surface, known as reflective scattering, whilst the fourth type consists of a single material with an absorption band similar to that of the terrestrial solar spectrum.

2.2.1 SELECTIVE SINGLE MATERIALS

It is theoretically possible to produce a surface that selectively absorbs solar radiation. In fact black molybdenum coated with a silicon nitride layer, to protect the film, has been shown to have a solar absorptance of 0.94 and thermal emittance of 0.11 and has proved to be stable (in a vacuum) at 500°C for several thousand hours. Unfortunately its high cost and only moderate efficiency make this material only

academically interesting.

Work has been done in producing spectrally selective surfaces from a material composed of metal carbides and nitrides but the moderate absorptances and thermal emittances render these surfaces practically useless for use at temperatures of around 300°C. These materials seem, however, more promising for operating temperatures above 700°C because these compounds are refractory.

Attempts have also been made to utilize semiconductors like amorphous silicon. Unfortunately, semiconductor oxides, sulfides, selenides and tellurides, titanium nitrides and carbides/16/, hafnium carbides and metal borides only approximate the desired spectral cut-off at 2 μ m.

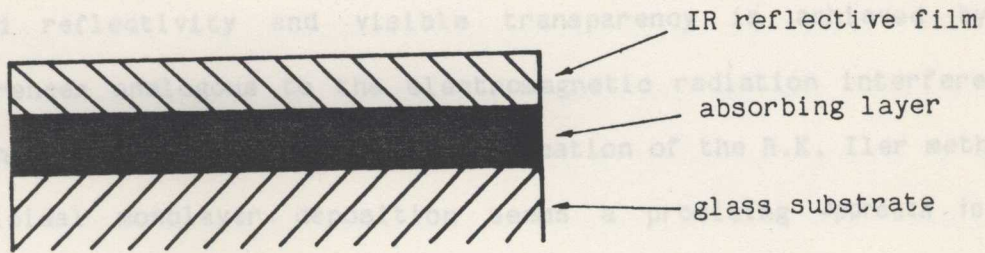
2.2.2 SCATTERING SURFACES

In 1955 Tabor was the first person to realise that scattered light interferences due to surface roughness could produce a solar absorber. Surface textures on metals /8,10/ could for example discriminate between the small wavelength character of the incident solar radiation and the large hemispherical wavefront of thermal radiation. Spectral selectivity is then obtained when the geometry of the textured surface is of the order of the wavelength of light, resulting in absorption of the visible region but reflection for longer wavelengths.

In fact many collectors owe their absorptance enhancement to surface roughness /9/. This effect is most helpful in cases where the increase in solar absorptance is more important than the small increase in the emittance. Unfortunately, surface roughness alone is not enough since only moderate absorptances and thermal emittances have been obtained.

2.2.3 HEAT MIRRORS

FIGURE 2.2



Heat mirrors consist of semi-transparent metal films or of metal films made antireflecting by dielectric layers on either side, on top of an absorbing film. Unfortunately, the achievement of high solar transmittance is limited by the need to achieve suitable relative values of the optical constants of the metal and the dielectric layers. Molybdenum films, however, provide a good match but the reflectance occurs at $10\mu\text{m}$ and not $2\mu\text{m}$.

Heavily doped semiconductors with a band gap in the ultraviolet ensure infrared reflectance. Films of stannic oxides, tin-doped indium oxides and indium-niobium doped Cadmium stannates are a few examples of systems which, when sprayed onto amorphous silicon (the absorber), are stable at temperatures up to 300°C , adhere well to glass and resist environmental attack. Proper choice of doping can boost infrared reflectance at the expense of visible transmission or visa-versa, but efforts are being made to improve the transparency.

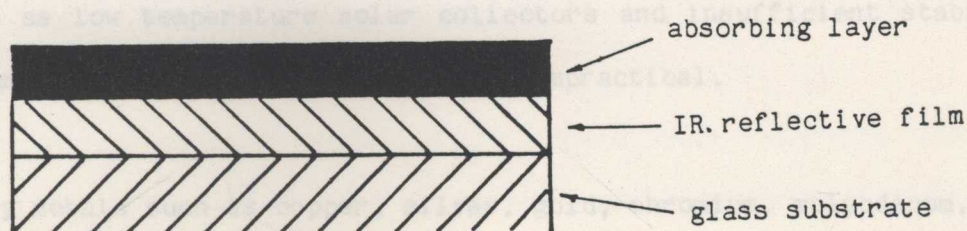
Even though there are problems of achieving good selectivity for both metals and highly doped semiconductors, flat plate collectors with almost non-selective inexpensive absorbers can be upgraded by mounting the surface behind a cover glass or enclosure of high infrared reflectance.

2.2.4a INTERFERENCE FILTERS

Future research into titanium oxide and silica layers (called tandems) may result in cheap surfaces produced from colloidal solutions whose infrared reflectivity and visible transparency is achieved by light interferences analogous to the electromagnetic radiation interferences of electronic band pass filters. The application of the R.K. Iler method /14/ of colloidal monolayer deposition seems a promising approach to these tandems.

2.3.4 DARK MIRRORS

FIGURE 2.3



The most popular solar selective design is the Dark Mirror because it is capable of achieving high absorptances with low thermal emittances /23,24,26/ and there exist surfaces that have excellent efficiencies, for domestic uses, at very low cost /21/. Spectral selectivity is achieved by the absorption of the top layer and infrared reflectance from the metal substrate (usually copper) underneath.

Three general types of absorbing layers are commonly studied and used and in them absorption is usually achieved by metal oxides, small metal particles in a dielectric host (called cermet) or by interference effects of alternating metal and dielectric films.

2.2.4a INTERFERENCE FILTERS *major drawbacks.*

The theory of obtaining absorption by interference effects from alternating metal and dielectric layers is well understood /15,17/ and producing these layers by vacuum techniques has already been achieved. Alas, one of the difficulties in obtaining a desirable surface is finding materials which possess matching optical properties that will result in an efficient absorber. A silver-alumina-chromium-alumina (on copper) layered tandem has been shown to exhibit absorptances from 0.90 to 0.95 and thermal emittances as low as 0.02 to 0.04; tests on the system have shown no deterioration after 1000 hours at 150°C in air or for brief periods at 600°C in a vacuum. Unfortunately the relatively high cost of production for use as low temperature solar collectors and insufficient stability at high temperatures render these surfaces impractical.

One day solidly deposited monolayers (see reference 14) may be
Many metals such as copper, silver, gold, chromium, molybdenum, nickel, iron, tin, titanium and dielectrics such as magnesium fluoride, silica, alumina and cesium dioxide have been studied whilst metal carbides too have been investigated. Unfortunately, for most designs either high costs of production, high temperature instability or moderate absorptance/emittance efficiencies of these surfaces has hindered any large scale manufacture of these types of absorbers for use as solar selective coatings. *all which have*

higher solar conversion efficiencies (than ungraded coatings) /9,23,24,
The limitations of these surfaces can be summarised as follows: *limitations*
are the major drawbacks.

(i) These absorbers can be considered as a "tuned optical cavity" where detuning and degradation can occur due to molecular reorientation from the effects of high temperatures. Although the alumina-molybdenum-alumina tandem has been shown to be stable (for 24 hours only) at 500°C its moderate absorptance (0.85), rather high thermal emittance (0.11) and the

high cost of molybdenum are the major drawbacks.

Corrosion at the surface of these absorbers from environmental or chemical attack can spoil the balance of partial reflectances whilst diffusion across the interfaces can change the optical constants.

(ii) Compatibility of thermal expansions and chemical reaction inertness between the layers is critical. This results usually in the use of rare and expensive materials.

(iii) At this stage the vacuum techniques which have usually been used lead to restrictions with respect to large scale fabrication, though chemical vapour deposition has been tried successfully for some materials.

One day colloiddally deposited monolayers (see reference 14) may be possible for these systems, but there are some restrictions to this method (see section 3.1).

(iv) The films are sensitive to the angle of incident radiation therefore the effectiveness of the interference filter is reduced.

(v) Graded refractive index coatings can be fabricated which have higher solar conversion efficiencies (than ungraded coatings) /9,23,24, 30-4/ but the high costs of production and high temperature instabilities are the major drawbacks.

2.2.4b METAL OXIDE FILMS

Copper oxide /18,19,21,47,48/ and chromium oxide (chrome black) /44,45/ films are the two more popular types of absorbers (where some of the

absorption is due to surface roughening i.e. surface scattering interferences) on metal substrates, though other metal oxides have also been investigated /29/. The oxidation processes for producing these surfaces can be economical for large scale fabrication and most oxides exhibit moderate selectivity at low operating temperatures ($0.60 \leq a_s \leq 0.85$, $0.10 \leq e_t \leq 0.40$). In the case of copper (and steel) the Ebanol treatment (trade name of Enthone Inc., New Haven, Connecticut) achieves absorptances from 0.80 to 0.90 and thermal emittances usually from 0.15 to 0.20, although an emittance as low as 0.07 has been reported. Evidently Ebanol-C produces a surface with a dendritic structure which increases solar absorptance and surface stability.

(iii) change in the surface texture by producing pores and voids (see next section). Here in Australia, C.S.I.R.O. and Rheem Aust.Pty Ltd have developed a protective coating for copper oxide films known as the AMCRO process /21/. The AMCRO coating $((\text{NH}_4)_2\text{CrO}_4 \cdot (\text{CuCrO}_4)_2 \cdot (\text{Cu}(\text{OH})_2)$ not only protects the copper oxide film from degradation but increases the absorptance to 0.94 and decreases the thermal emittance to 0.08. Unfortunately this absorbing surface is unstable when held at temperatures above 150°C for extended periods of time, and is only useful for domestic purposes (i.e. operating temperatures of around 75°C).

As with all types of Dark Mirrors the layer thickness of metal oxide absorbers is critical. The heating and dipping of metals to form metal oxide surfaces can lead to variations of film thickness and substrate impurities. Excepting the AMCRO and Ebanol processes, diffusion effects, material phase changes and general instability /21/ due to environmental corrosion are the main disadvantages of metal oxide films. The low cost of production, however, more than compensates for this.

Some interest has been shown for chrome black coatings in preference to

copper oxide films because of the enhanced selectivity of the former ($a_s \approx 0.96$, $e_t \approx 0.07$) even though the cost of production is greater. The chief method of production of chrome black is by electrodeposition. A big advantage of electroplating is that by the control of conditions of the plating bath one can increase the efficiencies of an absorbing surface by:

2.3 COLLECTOR CONFIGURATION

(i) variation of the composition of the film in producing interference filters (see section 2.2.4a)

(ii) variation of the refractive index (see section 4)

(iii) change in the surface texture by producing pores and voids (see section 2.2.2)

The moderate cost of production by electroplating entices many manufacturers into making chromium oxide absorbers but unfortunately the low durability of chrome black at high temperatures /42,44,45/ is a major drawback for more efficient collectors. Also the process control limits that are adequate for decorative chrome blacks are insufficient for solar coatings and as well there is very little control in continually manufacturing stable coatings.

The most popular photothermal solar collector design is the "flat plate" design (see figure 2.5). This popularity is due to the simplicity and low cost of manufacturing this type of collector.

2.2.4c CERMET LAYERS

More will be said about cermets in section 4 but basically the cermet absorber consists of small metal (or conducting) particles embedded in a dielectric medium /7,23-8,35-43/. Grading the refractive index of the film by producing a metal rich concentration near the substrate to a dielectric rich surface has been shown to improve the selectivity further /9,23,24,30-4/. The main advantages of cermet absorbers lie in the high

absorptances and low thermal emittances obtained (e.g. $a_s = 0.93$, $\epsilon_t = 0.035$ /23,24/), good stability at high temperatures /25,28,36,43,46/ and the possibility of producing a cheap yet moderately efficient, stable surface. One such surface is the subject of this thesis.

2.3 COLLECTOR CONFIGURATION

The main objective of the solar collector is to maximise the absorption of the incident solar flux. Unfortunately, heat losses are incurred by reflective losses from the collector cover and conductive, radiative and reflective losses from the absorbing surface (see figure 2.4). The radiative and reflective heat losses can be minimised by fabricating highly spectrally selective surfaces (see previous sections) and antireflection coatings (see section 6) respectively. However, reducing conductive heat losses from the absorbing surface requires that the surface be enclosed in an evacuated chamber. Convection Suppression Devices /22/ (i.e. thin sheets of teflon) can also reduce conductive heat losses but are not as efficient as evacuated chambers and they have the disadvantage of reducing the intensity of the solar flux incident to the surface because of their slight opacity.

The most popular photothermal solar collector design is the "flat plate" collector (see figure 2.5). This popularity is due to the simplicity and low cost of manufacturing this type of collector. Unfortunately, the difficulty of concentrating (or magnifying) the solar flux incident to the absorbing surface and the inability to encase the solar selective surface in an evacuated chamber are the two major disadvantages of this type of design.

FIGURE 2.4 LOSSES FROM THE INCIDENT SOLAR RADIATION BY THE
PHOTOTHERMAL COLLECTOR

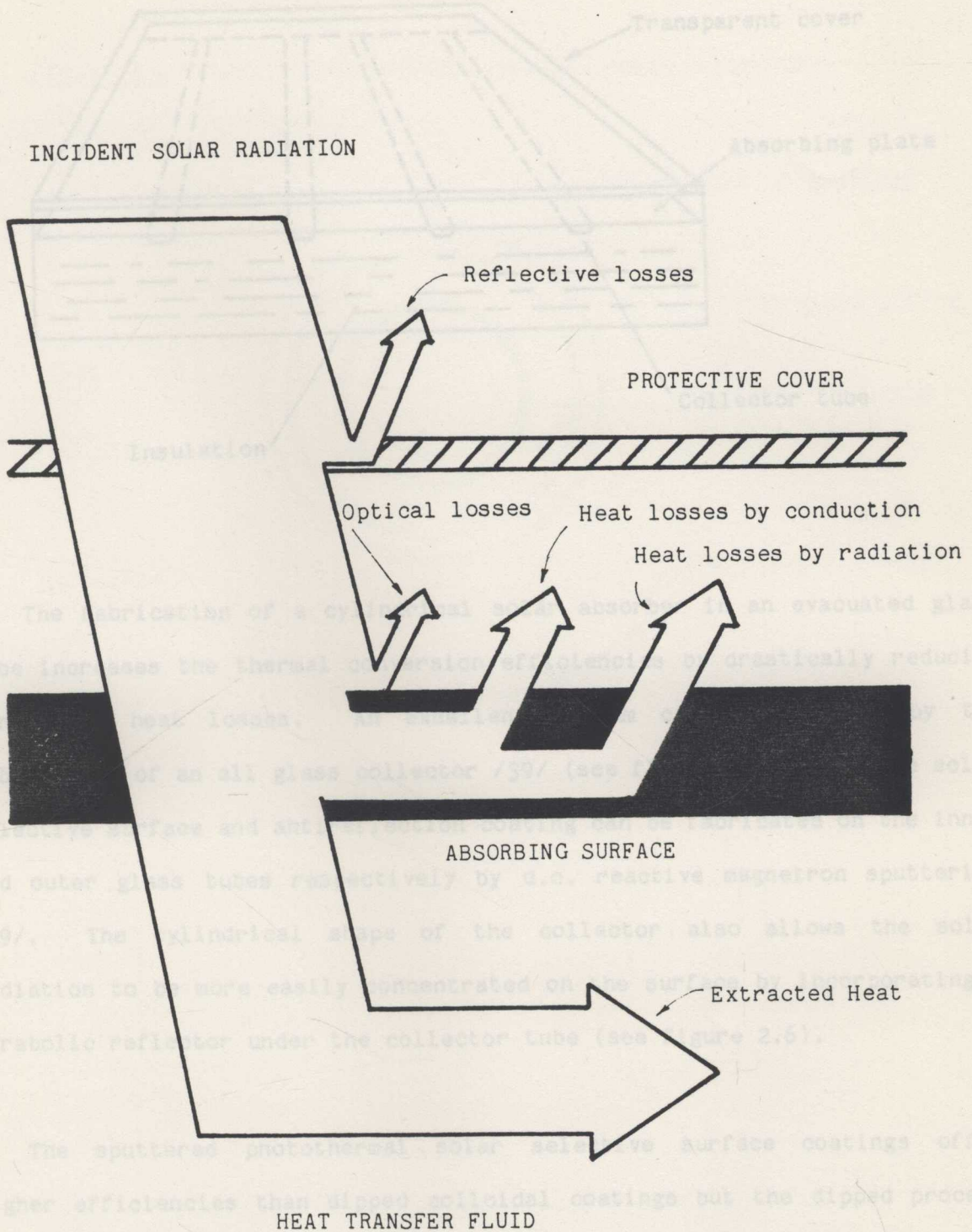
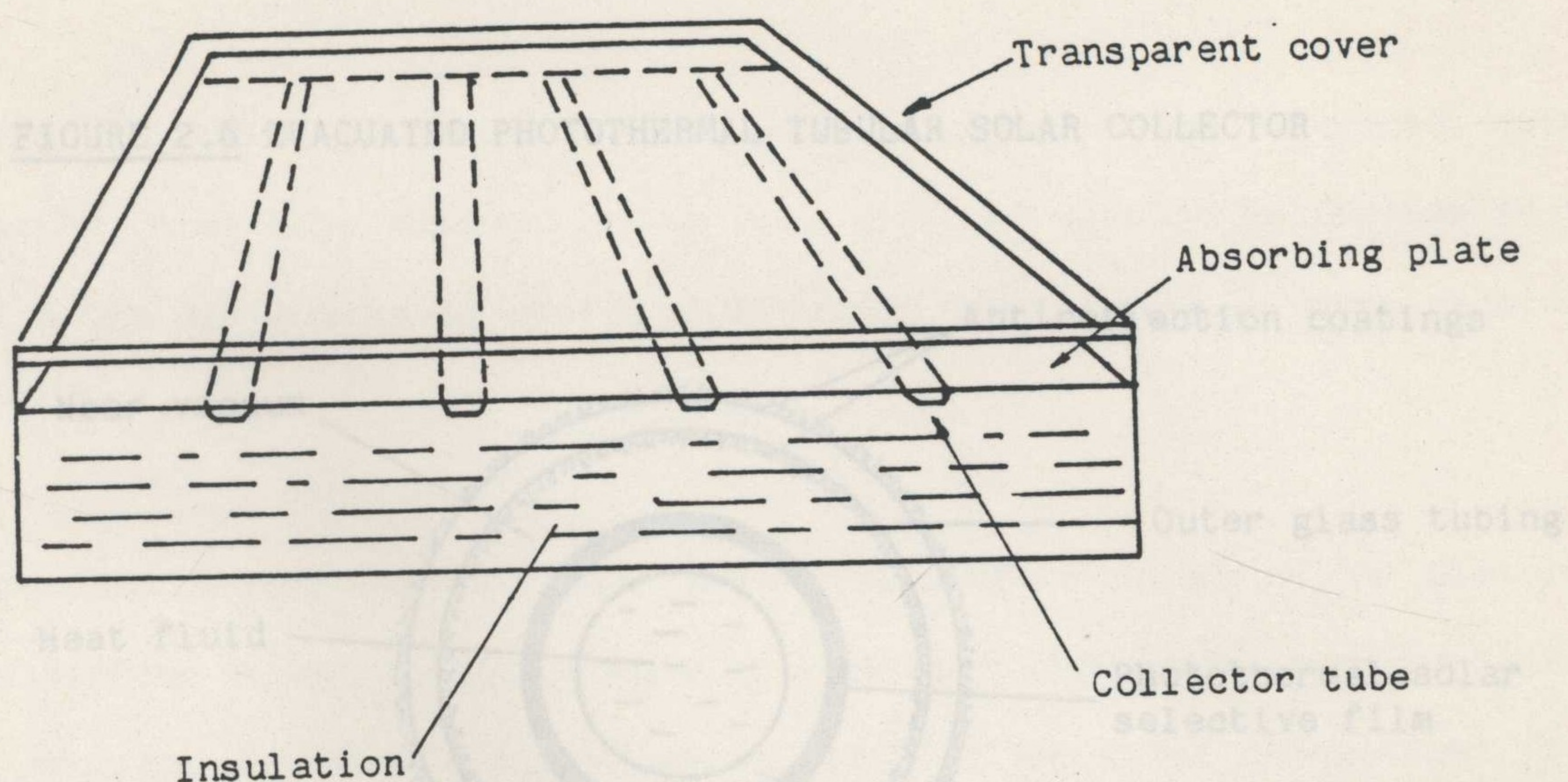


FIGURE 2.5 FLAT PLATE COLLECTOR



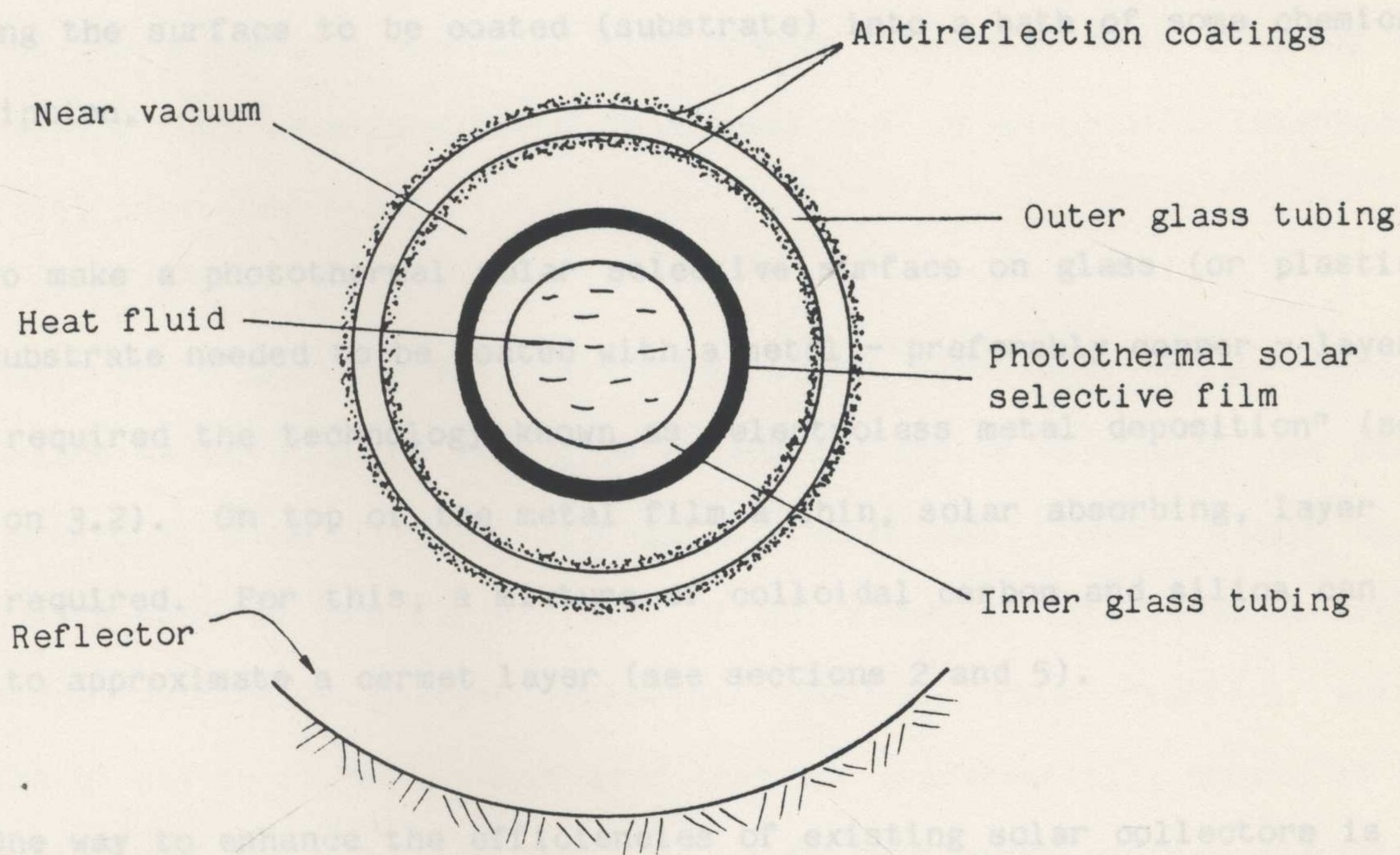
The fabrication of a cylindrical solar absorber in an evacuated glass tube increases the thermal conversion efficiencies by drastically reducing conductive heat losses. An excellent vacuum can be achieved by the fabrication of an all glass collector /39/ (see figure 2.6) where the solar selective surface and antireflection coating can be fabricated on the inner and outer glass tubes respectively by d.c. reactive magnetron sputtering /49/. The cylindrical shape of the collector also allows the solar radiation to be more easily concentrated on the surface by incorporating a parabolic reflector under the collector tube (see figure 2.6).

The sputtered photothermal solar selective surface coatings offer higher efficiencies than dipped colloidal coatings but the dipped process for fabricating colloidal antireflection films has the advantage of coating both sides of the outer glass cover with one dip and the resulting tandem has been shown to exhibit excellent antireflection properties (approximately 2% /174/). This would lead to the viability of coating previously sputtered tubular solar cells with colloidal antireflection films by a simple and

cheap dipping process, hence increasing the solar converting efficiencies

with a minimum of effort.

FIGURE 2.6 EVACUATED PHOTOTHERMAL TUBULAR SOLAR COLLECTOR



3.1 COLLOIDS

3.1.1 WHAT IS A COLLOID?

The name "colloid" means "gum-like" and was given by Thomas Graham in the mid nineteenth century. The "gum-like" substances he studied were some polysaccharide gums whose molecular sizes were very much larger than the solvent molecules. As a result, groups of molecules or particles whose sizes (typically 1 nm to 1000 nm) are much larger than the sizes of the solvent molecules (typically a few angstroms) are regarded as colloids. Some examples of colloidal systems are: smoke, hairspray, mist, fog.

SECTION 3

PRODUCING AN EFFICIENT SOLAR SELECTIVE SURFACE TOTALLY FROM CHEMICAL BATHS

The intention of this project was to produce an efficient solar collector using only chemical baths i.e. coatings were to be fabricated by dipping the surface to be coated (substrate) into a bath of some chemical description.

To make a photothermal solar selective surface on glass (or plastic) the substrate needed to be coated with a metal - preferably copper - layer. This required the technology known as "electroless metal deposition" (see section 3.2). On top of the metal film a thin, solar absorbing, layer is also required. For this, a mixture of colloidal carbon and silica can be used to approximate a cermet layer (see sections 2 and 5).

One way to enhance the efficiencies of existing solar collectors is to fabricate an antireflection coating on the outer protective glass cover by dipping the glass into a bath containing colloidal silica (see section 6).

3.1 COLLOIDS

3.1.1 WHAT IS A COLLOID?

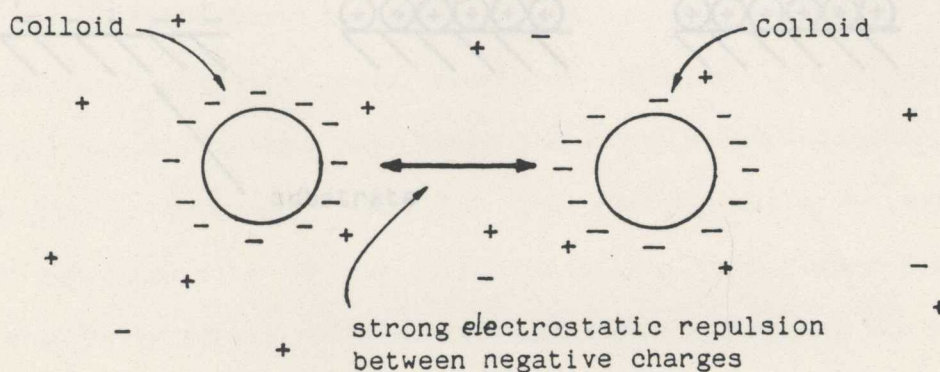
The name "colloid" means "gum-like" and was given by Thomas Graham in the mid nineteenth century. The "gum-like" substances he studied were some polysaccharide gums whose molecular sizes were very much larger than the solvent molecules. As a result, groups of molecules or particles whose sizes (typically 1 nm to 1000 nm) are much larger than the sizes of the solvent molecules (typically a few angstroms) are regarded as colloids. Some examples of colloidal systems are: smoke, hairspray, mist, fog,

printing ink, paint, milk, mayonnaise, fire-extinguisher foam, ruby glass, some metal alloys, ice cream and insulating foam.

The interesting and special features of a colloidal system are due primarily to the large surface area of contact of the colloid with a solvent (or dispersion medium). The energy associated with creating and maintaining that interface leads to a great deal of study into interfacial (surface) chemistry /50/.

Many colloidal systems involving solid particles in an aqueous dispersion medium require some type of surface active substance that stops the particles from forming aggregates (after collisions) which would eventually lead to one large "lump" of solid matter instead of a nicely dispersed colloidal system (colloidal sol). This "surface active substance" may be in the form of ions that are preferentially bonded to the surface of the colloid, such that collisions that could produce aggregates would be reduced significantly due to electrostatic repulsions (see figure 3.1). Another "surface active substance" may be polymers that bond to the colloidal surface where the tail of the polymer is either large and bulky, causing steric hindrance, or charged, causing electrostatic repulsions.

FIGURE 3.1 ELECTROSTATIC REPULSION BETWEEN COLLOIDS



3.1.2 THE ILER METHOD

FIGURE 3.6

In 1969 R.K. Iler published a patent /14/ that suggested surface coatings could be produced by successive monolayers of oppositely charged colloids. The method consisted of first dipping a substrate (that has an associated surface charge when immersed in an aqueous solution e.g. copper which has a negative surface charge when immersed in a dilute acidic solution) into a colloidal sol with colloids of a surface charge of sign opposite to the substrate surface charge (i.e. a positive charge). When immersed, the colloids would then be electrostatically bonded to the substrate (see figure 3.2). Upon removal of the coated substrate, and subsequent rinsing, the substrate would then have a monolayer coating of the colloid and a new positive surface charge (see figure 3.3). To produce a second monolayer the coated substrate would then be immersed into a colloidal sol where the colloids possessed a negative surface charge (see figure 3.4). When withdrawn and then rinsed the surface would carry an additional coating with a negative surface charge (see figure 3.5). This procedure could be repeated so as to produce coatings of any thickness required (see figure 3.6).

FIGURE 3.2

FIGURE 3.3

FIGURE 3.4

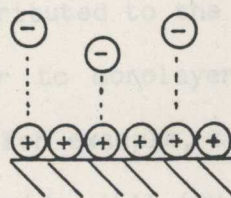
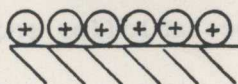
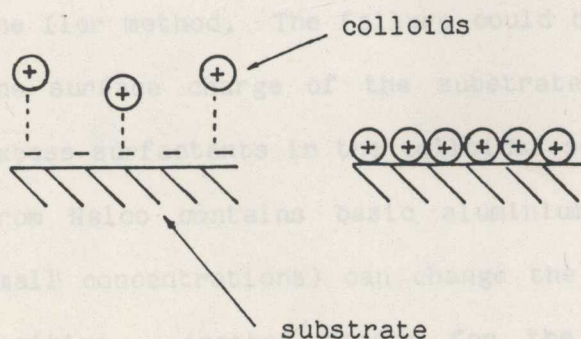


FIGURE 3.5

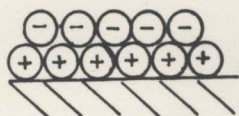
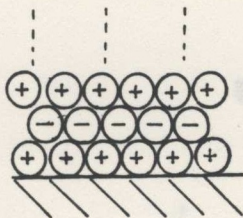


FIGURE 3.6

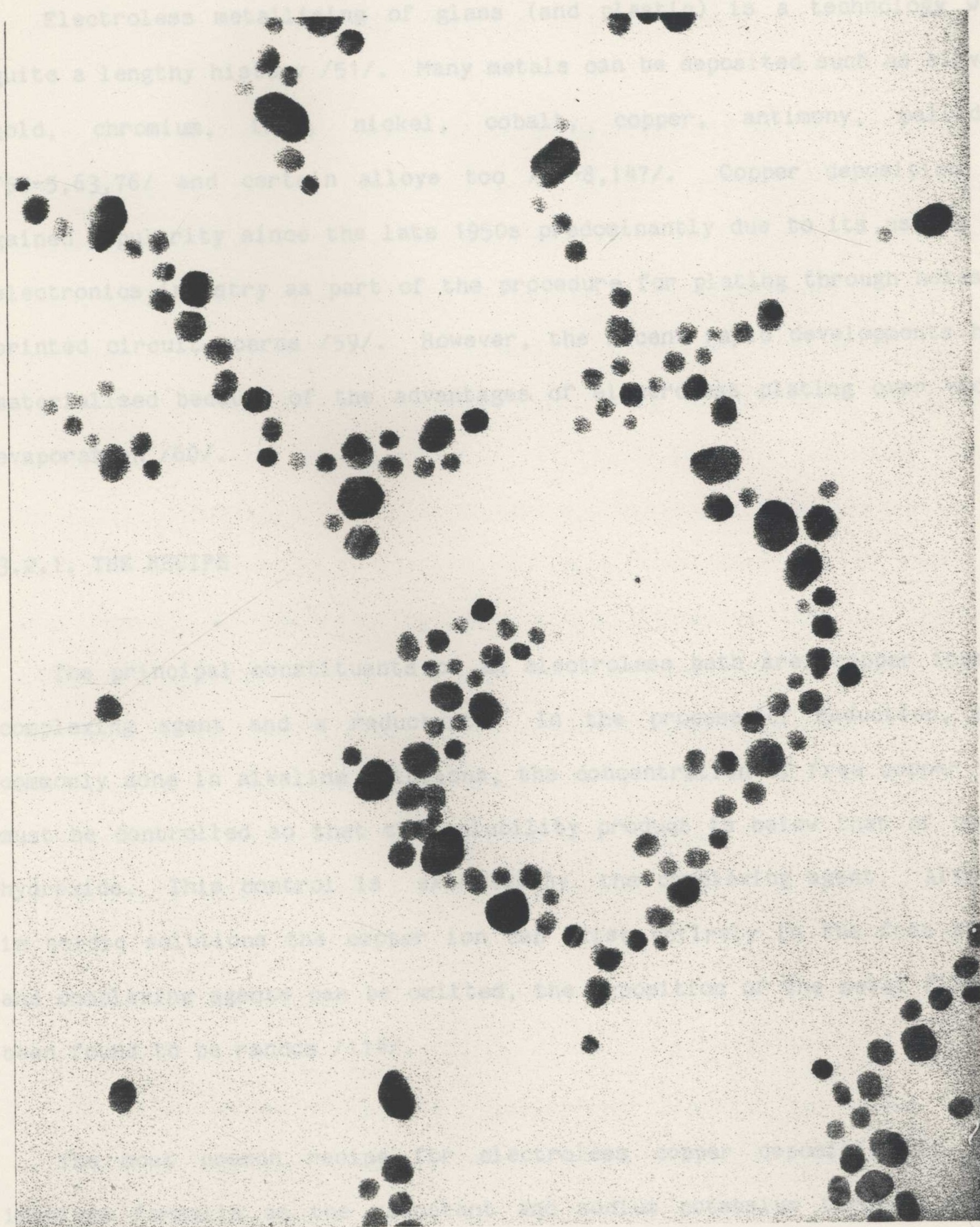


Lendrum (1981 /151/) attempted to produce a photothermal solar selective ("Interference" type, see section 2.1) surface using the Iler method. The substrate used was copper and the colloids were silver and silica. To fabricate a photothermal solar selective surface, positively and negatively charged colloidal silver and silica were required. The production of colloidal silver with a negative surface charge involved the reduction of silver ions by sodium borohydride /152/, positively charged colloidal silver was obtained by the addition of N-cetyl-trimethylammoniumbromide (CTAB). Silica with a negative surface charge was obtained from Du Pont Chemicals Pty Ltd Aust. and silica with a positive surface charge was obtained from Nalco Chemical Company, Chicago, Illinois, U.S.A.

Unfortunately, little success was achieved in this project in repeating the Iler method. The failure could be attributed to the neutralisation of the surface charge of the substrate prior to monolayer addition due to excess surfactants in the colloidal sols. For example, the silica obtained from Nalco contains basic aluminium chloride ($[Al_2(OH)_5Cl]_x$) which (at small concentrations) can change the negative surface charge of silica to positive. Another reason for the failure could be explained by the non-monodispersity of the colloidal silver (see figure 3.7) resulting in uneven layer formation (i.e. islands), when attempting the Iler method, and

FIGURE 3.7 COLLOIDAL SILVER /184/

3.2 ELECTROLESS COPPER DEPOSITION



50 nm

hence a coating with areas of positive and negative charges.

3.2 ELECTROLESS COPPER DEPOSITION

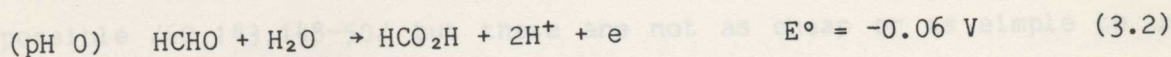
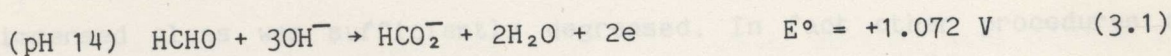
Electroless metallising of glass (and plastic) is a technology with quite a lengthy history /51/. Many metals can be deposited such as silver, gold, chromium, iron, nickel, cobalt, copper, antimony, palladium /52-5,63,76/ and certain alloys too /56-8,147/. Copper deposition has gained popularity since the late 1950s predominantly due to its use in the electronics industry as part of the procedure for plating through holes of printed circuit boards /59/. However, the recent rapid developments have materialised because of the advantages of electroless plating over vacuum evaporation /60/.

3.2.1. THE RECIPE

The principal constituents of an electroless bath are: copper ions, a complexing agent and a reductant. In the process of reduction, most commonly done in alkaline solutions, the concentration of free copper ions must be controlled so that the solubility product is below that of copper hydroxide. This control is exercised by the complexing agent. Although in acidic solutions the copper ion can exist entirely in the free state, and complexing agents can be omitted, the deposition of the metal film has been found to be random /114/.

The most common recipe for electroless copper deposition on glass involves formalin as the reductant and sodium potassium tartrate as the complexing agent /51,53,60,115-8/. When using formalin it has been shown that copper reduction is best done under basic conditions because the electrode potential for the oxidation of formaldehyde is more positive at a

pH of 14 than that at a pH of 0 /53,119,120/, as seen by these two equations:



Apart from formalin, sodium borohydride /128,129/ and hydrazine hydrate /51,118,119,130,134,147/ are two more popular reducing agents, whilst dimethylamine borane /56/, sodium sulphite /135/, hydroxyethylhydrazine /136/, hydrazine borane /95/ and alkali metal cyanoborohydrides /137/ have also been investigated but unfortunately these are not as cheap or as simple to use as formalin. Many complexing agents other than sodium potassium tartrate /51,56,71,82,94,111,136-41,144-7/, including ammonia /51,95,116,118,119,130,133,134,136,138/ and ethylenediaminetetraacetic acid (EDTA) /56,64,73,82,88,99-101,142,147/ have been used but it seems that when formalin is the reducing agent sodium potassium tartrate (otherwise known as Seignette salt or Rochelle salt) is the more compatible in cost and plating rate efficiency. Many attempts have been made to introduce economies into the electroless procedure by the use of stabilisers and various other additives /61-113/ but in general these are only small improvements though significant in industry.

3.2.2 SURFACE ACTIVATION

A major breakthrough in electroless plating has been due to "activating" the glass, resulting in uniform and pure films. In fact the formalin bath recipe, which remains stable (without additives) for a lengthy period of time, will not plate if the surface to be coated is not treated properly. Earlier attempts primed the glass (or plastic) with silver or silver oxides /51,115,121/. Unfortunately these did not give

consistent results, but by immersing the glass into dilute acidic solutions of stannous chloride then palladium chloride /56,116,117/ magnificent conductive and adherent /60/ films are obtained, providing that the immersed glass was sufficiently degreased. In fact other procedures are possible /60,143,148-50/ but these are not as cheap or as simple to use. One disadvantage with this type of plating is that the film can only obtain a thickness of about 100 nm before it appears to "blister" hence rendering the coating useless. Many authors attribute this phenomenon to the formation of hydrogen gas under the copper film /118-20,123,124/ according to the equation:



Nevertheless before blistering of the film occurs a conductive coating is formed which in turn can be made thicker by electroplating /51,60/.

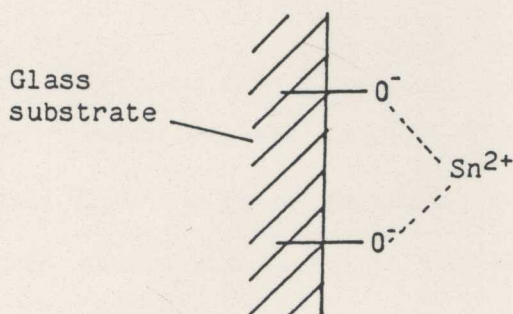
The mechanism of electroless copper deposition is not well understood; in fact most of the published work involves modifications of existing recipes. It is, however, a popular belief that the "activation" of the surface produces a catalyst for the formation of the metallic film and the evolution of hydrogen gas. Although the reduction of copper to the metallic state is thermodynamically possible, it is likely that the activation energy for the process (using the formalin recipe in the absence of a catalyst) is too high /53,120,123/. Just recently some workers /125/ have analysed the surface of a carbon coated collodian prior to a copper electroless plating, using the stannous chloride and palladium chloride activating procedure previously mentioned, and they discovered the existence of stannic oxide particles, after stannous chloride sensitisation, and the formation of cuprous oxide particles just prior to the copper film deposition. Unfortunately little mention is made of

the existence of colloidal palladium during this procedure /60,114,120/. Studies on the rates of copper metal deposition have also been made /56,60,118,123/ some with the intention of postulating a mechanism for this deposition, with little success /126,127/. Other workers have implied that the resulting roughness of the surface is the main reason for the adhesion of the film /60/; that is, the stannic oxide and palladium particles fit into the pores of the substrate like the pieces of a jigsaw puzzle. Understanding of the processes behind electroless copper plating is still far from being resolved.

3.2.3 MECHANISMS FOR GLASS ACTIVATION

When a clean glass substrate is immersed into a stannous chloride/hydrochloric acid solution (pH 1) it is possible for some of the stannous ions to adhere to the oxide groups on the glass surface (see figure 3.8)

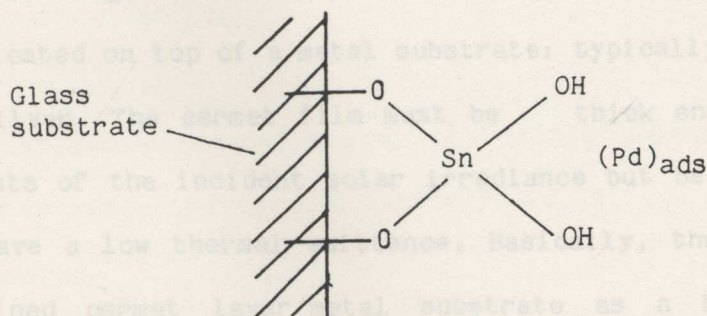
FIGURE 3.8



When immersing this "tin-activated" glass slide into a solution

containing palladium chloride and hydrochloric acid (pH 3) a redox reaction may occur between the stannous complexes and palladium ions resulting in (stable) stannic hydroxide complexes on the glass surface with adsorbed palladium colloids (see figure 3.9)

FIGURE 3.9



More research is needed in this field of study so as to understand more about the chemistry of electroless metal deposition. Resulting in poor selectivity. Typically the cermet layer thickness is of the order of 10^{-7} m (wavelength of visible light) and is therefore thin enough to be transparent to infrared radiation (long wavelength).

4.3.1 MAXWELL GARNETT THEORY

The Maxwell Garnett theory /153,154/ can describe the cermet layer providing that the metal particles are very small compared to the incident radiation wavelength (i.e. no scatter) and that the concentration of the metal particles is low (i.e. negligible dipole-dipole interactions), though corrections for deviations from these conditions have been attempted /7/. Another medium theory exists (known as the Bruggeman theory /155/), however, the Maxwell Garnett theory is preferred because it is derived from first principles and the geometry to which it applies is well defined.

SECTION 4

THE CERMET DARK MIRROR TANDEM

4.1 CERMET LAYERS

The cermet layer consists of small metal particles embedded in a dielectric host. To achieve selectivity (i.e. high absorption in the visible range and reflection in the infrared region) the cermet layer is fabricated on top of a metal substrate: typically copper, aluminium, nickel or silver. The cermet film must be thick enough to absorb substantial amounts of the incident solar irradiance but be as thin as possible so as to have a low thermal emittance. Basically, the radiation must "see" the combined cermet layer/metal substrate as a homogeneous film with the desirable absorption characteristics of the cermet layer and infrared reflectance of the metal substrate. If the cermet layer were too thick then the combined cermet/metal film would approach the properties of a cermet film alone and hence have a high thermal emittance resulting in poor selectivity. Typically the cermet layer thickness is of the order of 10^{-7} m (wavelength of visible light) and is therefore thin enough to be transparent to infrared radiation (long wavelength).

4.1.1 MAXWELL GARNETT THEORY

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4.1.1a EXPRESSIONS FOR OPTICAL CONSTANTS OF MEDIA CONTAINING METAL IN AN AMORPHOUS FORM

The Maxwell Garnett theory describes the effective medium to consist of metal spheres embedded in an isotropic non-absorbing matrix. When deriving this theory it is first useful to consider the macroscopic polarisation of the effective medium.

Polarisation is defined as the dipole moment per unit volume. When a medium is subjected to an electric field, $\underline{E}$, the resulting polarisation, $\underline{P}$, is given by:

$$\underline{P} = \epsilon_0 X \underline{E} = \epsilon_0 (\epsilon - 1) \underline{E} \quad (4.1)$$

where ϵ_0 is the permittivity of vacuum, X is the electric susceptibility and ϵ is the relative permittivity or dielectric constant.

The macroscopic polarisation can also be determined from microscopic considerations. Imagine a dielectric media consisting of many molecules in vacuo. Consider that this dielectric is placed between two parallel capacitor plates of infinite size: resulting in zero end effects. Visualise one of the molecules of this dielectric as inside a sphere. Inside this sphere individual molecules are considered (microscopically) yet outside the sphere the surrounding medium is homogeneous with macroscopic properties. The molecule is therefore influenced by fields arising from:

- (i) the charges on the interior of the capacitor plates
- (ii) the surface charge on the dielectric facing the capacitor plates
- (iii) the surface charge on the interior of the spherical boundary

(iv) the charges of the individual molecules, other than the molecule under consideration, contained within the sphere; since the dielectric is isotropic this contribution is zero.

Consider a sphere of radius, a , in a uniform electric field (in vacuum) and This leads to /156/: location of point charges at a distance, r_0 , from the centre of this sphere, where $r_0 \gg a$ and a is much smaller than the wavelength of $\underline{E}_m = \underline{E} + (\underline{P}/3\epsilon_0)$ (see section 4.1.1c). One then (4.2) the induced field outside the sphere as that of a dipole whose moment is /156/:

where $\underline{E}_m$ is the field acting on the molecule.

$$\underline{E} = 4\pi\epsilon_0 a^3 ((\epsilon_s - 1)/(\epsilon_s + 2)) \underline{E}_0 \quad (4.5)$$

Now consider the induced dipole moment of this molecule in the dielectric as: ϵ_s is the dielectric constant of the sphere and $\underline{E}_0$ is the electric field at r_0 . The overall polarisation of a medium consisting of these

spheres spaced $\underline{P} = \alpha\epsilon_0 \underline{E}_m$ each other is: (4.3)

where p is the dipole moment and α is the polarisability of this molecule. For an amorphous medium consisting of many molecules, the overall polarisation of this medium is given by:

is analogous to the case presented earlier for the field acting on a molecule) is:

$$\underline{P} = Np \quad (4.4)$$

$$\underline{E}_0 = \underline{E} + (\underline{P}/3\epsilon_0) \quad (4.5)$$

where N is the number of molecules per unit volume.

$$\underline{E} = (1 - 4\pi Na^3 (\epsilon_s - 1)/3(\epsilon_s + 2)) \underline{E}_0 \quad (4.6)$$

Substituting into equation 4.2 and using equation 4.1 the following relation is obtained: ϵ and 4.1 and substituting:

$$(\epsilon - 1)/(\epsilon + 2) = N\alpha/3 \quad (4.5)$$

then:

otherwise known as the Clausius-Mossotti relation. (4.10)

4.1.1b EXPRESSIONS FOR OPTICAL CONSTANTS OF A MEDIUM CONTAINING METAL PARTICLES

Consider a sphere of radius, a , in a uniform electric field (in vacuo) and also consider the summation of point charges at a distance, r_0 , from the centre of this sphere, where $r_0 > a$ and a is much smaller than the wavelength of visible light (see section 4.1.1c). One then obtains the induced field outside the sphere as that of a dipole whose moment is $/156/$:

$$\underline{P} = 4\pi\epsilon_0 a^3 ((\epsilon_a - 1)/(\epsilon_a + 2)) \underline{E}_0 \quad (4.6)$$

where ϵ_a is the dielectric constant of the sphere and $\underline{E}_0$ is the electric field at r_0 . The overall polarisation of a medium consisting of these spheres spaced far from each other is:

$$\underline{P} = 4\pi N \epsilon_0 a^3 ((\epsilon_a - 1)/(\epsilon_a + 2)) \underline{E}_0 \quad (4.7)$$

So the field acting on the sphere (which is analogous to the case presented earlier for the field acting on a molecule) is:

$$\underline{E}_0 = \underline{E} + (\underline{P}/3\epsilon_0) \quad (4.8)$$

or

$$\underline{E} = (1 - 4\pi N a^3 (\epsilon_a - 1)/3(\epsilon_a + 2)) \underline{E}_0 \quad (4.9)$$

Combining equations 4.7 and 4.1 and substituting :

$$f_a = 4\pi N a^3 / 3 \quad (4.9a)$$

then:

$$(\epsilon - 1)/(\epsilon + 2) = f_a (\epsilon_a - 1)/(\epsilon_a + 2) \quad (4.10)$$

This is the Maxwell Garnett formula for metallic spheres, with a dielectric constant, ϵ_a , in vacuo.

To determine the optical constants for metal spheres in an isotropic medium (e.g. silica) of dielectric constant, ϵ_b , the relation:

$$\epsilon_b' = \epsilon' / \epsilon_b \quad (4.11)$$

is used, where ϵ_b' is the dielectric constant in silica and ϵ' is the dielectric constant in vacuo.

This then leads to:

$$(\epsilon - \epsilon_b) / (\epsilon + 2\epsilon_b) = f_a(\epsilon_a - \epsilon_b) / (\epsilon_a + 2\epsilon_b) \quad (4.12)$$

The above expression is the Maxwell Garnett equation used in many theoretical calculations of cermet layers. The terms ϵ and ϵ_a are commonly complex expressions, e.g.:

$$\epsilon = (n + ik)^2 \quad (4.12a)$$

with n the refractive index and k the extinction coefficient.

$$k = \alpha\lambda / 2\pi \quad (4.12b)$$

Typically, for metal particles approximately 5 nm in radius, ϵ_b is where n is the real refractive index, α is the absorption coefficient, λ is the wavelength (of light) and k is the extinction coefficient. ϵ_b , on the other hand, is usually assumed to be real only.

The above equation applies for spherical particles only but there are equations for ellipsoidal particles as well [7,35].

4.1.1c THE SIZE OF THE METAL PARTICLE

For equation 4.11 to be valid the size of the metal spheres must be much smaller than the wavelength of the incident radiation, otherwise the medium will no longer "appear" to be homogeneous to the incoming light; this will lead to scattering.

Consider the scattering cross-section, Q_s , and the absorption cross-section, Q_a , from the Mie theory (see reference 157), where:

$$Q_s = [64(\pi a)^4/3\lambda] \text{Re}[(\epsilon_a - \epsilon_b)/(\epsilon_a + 2\epsilon_b)]^2 \quad (4.13)$$

and

$$Q_a = 4\text{Im}[\pi a(\epsilon_a - \epsilon_b)/\lambda(\epsilon_a + 2\epsilon_b)] \quad (4.14)$$

where

$$I_s/I_o = \pi a^2 Q_s \quad (4.15)$$

and

$$I_a/I_o = \pi a^2 Q_a \quad (4.16)$$

where I_s , I_a and I_o are the intensities of the scattered, absorbed and incident radiation respectively, a is the radius of the metal sphere and λ is the wavelength of the incident radiation.

Typically, for metal particles approximately 5 nm in radius, I_s is negligible for incident radiation in the visible region.

4.1.2 THE GRADED REFRACTIVE INDEX OF THE CERMET LAYER

Work has been done /9,23,24,30-4/ that shows improved selectivity of cermet layers when the refractive index of the film varies from a high value at the metal substrate/cermet interface to a low value at the cermet

layer/vacuum(air) interface. This type of work has been questioned by Granqvist et al. /7/ who believe that refractive index grading may have no effect on the enhanced selectivity of the cermet (the example quoted was the Co/Al₂O₃ system) and suggest that alterations in the medium theory used could account for the reported improvements. /157/ (see section 2.1). In

fact copper appears to be the best candidate because it has over 98%

In relation to the mixed colloidal carbon and silica system, it is almost impossible to produce a cermet layer with a graded refractive index that could be accurately determined. As a result, this facet of the cermet layer is not dealt with in this thesis. From black collectors even though its

properties are much worse than silver, copper or aluminium. It is used

4.2 THE METAL SUBSTRATE manufacturing procedures (electroplating) for the

production of cheap black solar selective surfaces require nickel to be

The optical properties of bulk (or crystal) metal differ from that of the metal atom because the former no longer has bonded electrons but "free" or "plasma" electrons. These plasma electrons explain the high infrared reflectivity of the bulk metal.

Plasma electrons can be qualitatively understood when imagining the changes experienced by the outer-shell electron(s) of the metal atom as it transforms to be apart of the crystal structure of the bulk metal. In the single atomic state the electron(s) of the metal atom are bonded to the nucleus, but in metallic clusters the electrons are bonded to several metal nuclei. In the bulk metallic state the electrons no longer are bonded to any individual nucleus and hence exist as "pseudo free" point molecules (Drude electrons). The overall effect is a cloud of electrons filling the entire metal.

Theoretical evaluations /157/ have shown that the optical properties of the bulk metal give rise to high visible and infrared reflection and

absorption in the far ultraviolet and very low energy regions (eg conduction).

Not all metals can be used effectively as a good infrared reflector for the use in Dark Mirror Solar collector designs /157/ (see section 2.1). In fact copper appears to be the best candidate because it has over 98% reflectance above $2\mu\text{m}$ and is relatively cheap. Silver and aluminium are also good metals for this use but the former is far more expensive than copper and the latter does not have such a high reflectance. Nickel is a commonly used infrared reflector for chrome black collectors even though its properties are much worse than silver, copper or aluminium. It is used only because the existing manufacturing procedures (electroplating) for the production of chrome black solar selective surfaces require nickel to be the substrate /44/.

High solar selectivity (as copper) of such coatings /161-2/ and the enhancement of existing poorly selective surfaces by a thin layer coating of the colloidal mixture /163/. However these studies did not characterize the coatings in such a way as to predict the optimum carbon to silica ratio required.

Carbon has "metal-like" properties, i.e. electrical and heat conduction and hence colloidal carbon mixed with colloidal silica could approximate a perfect medium, whereby carbon represents the metal particles and the remaining colloidal silica/air what would represent the dielectric. If the carbon and silica colloids are small compared to the wavelength of the incident solar radiation and if the carbon is well dispersed, then the medium would appear to be homogeneous to the incoming light. As a result, it would be valid to apply the Maxwell Garnett theory to the medium.

If the Maxwell Garnett theory can then be shown to describe the mixed colloidal carbon and silica medium, then the optimum carbon to silica

SECTION 5

OPTIMISATION OF THE MIXED COLLOIDAL CARBON AND SILICA COATING.

As discussed previously (section 3.2.4) the cermet film on a high infrared reflecting metal is the most promising candidate for use as a photothermal solar selective surface. The disadvantages with the highly efficient sputtered coatings are the high capital cost of production equipment and instability at very high temperatures (above 400°C) /158-60/. Mixed colloidal carbon and silica coatings have been shown to be stable at high temperatures /161/ and offer an economic advantage over electroplated and sputtered coatings.

Previous studies on mixed colloidal carbon and silica coatings /161-3/ have reported the high solar selectivity (on copper) of such coatings /161-2/ and the enhancement of existing poorly selective surfaces by a thin layer coating of the colloidal mixture /163/. However those studies did not characterise the coatings in such a way as to predict the optimum carbon to silica ratio required.

Carbon has "metal-like" properties, i.e. electrical and heat conduction and hence colloidal carbon mixed with colloidal silica could approximate a cermet medium, whereby carbon represents the metal particles and the remaining colloidal silica/air host would represent the dielectric. If the carbon and silica colloids are small compared to the wavelengths of the incident solar radiation and if the carbon is well dispersed, then the medium would appear to be homogeneous to the incoming light. As a result, it would be valid to apply the Maxwell Garnett theory to the medium.

If the Maxwell Garnett theory can then be shown to describe the mixed colloidal carbon and silica medium, then the optimum carbon to silica

ratio could be determined (see section 5.3.2).

Should theoretical considerations fail in determining the optimum carbon to silica ratio, then the calculation of the effective absorptance efficiencies (thermal efficiency), a_m , for several films of varying thickness and carbon to silica weight ratios (see section 5.4) may lead to the determination of the best mixed colloidal carbon and silica coating.

5.1 PREPARATION OF THE COLLOIDAL SOLS

To fabricate a colloidal film that appeared homogeneous to solar radiation the colloids used would have to be as small as possible. The smallest colloidal silica available (as an aqueous dispersion with primary particle sizes ranging from 3nm to 5nm in diameter) was manufactured by Catoleum Aust. Pty. Ltd. (known as PR4850), and the smallest carbon black obtainable (in a powder form, with primary particle sizes in the range of 10nm to 13nm in diameter) was manufactured by Degussa Ltd., W.Germany (known as FW200). Unfortunately problems arose from using FW200 (which will be discussed in more detail later) and as a result "Special Black 4" made by Degussa (primary particle size of about 25nm in diameter) was used instead.

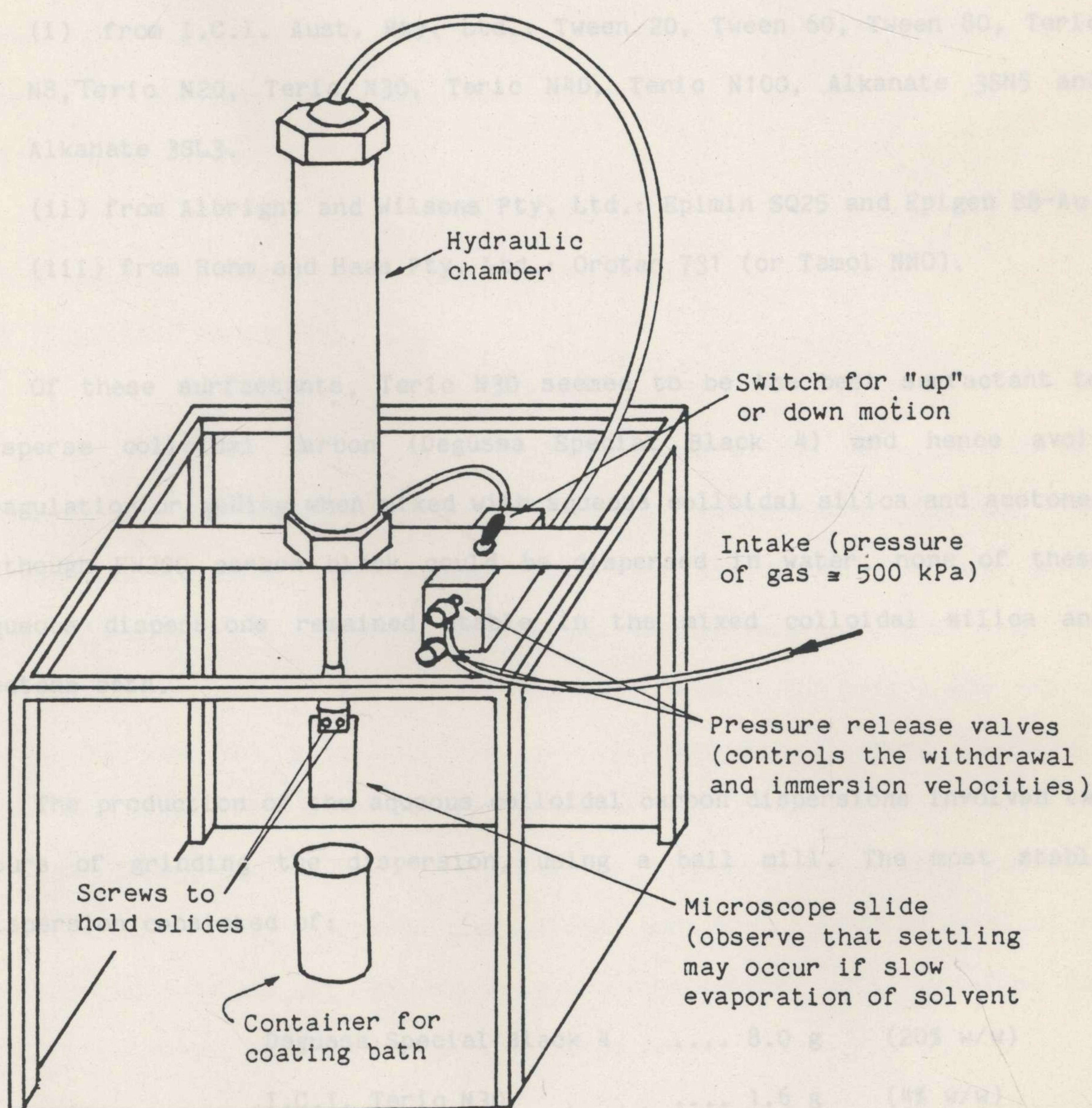
The fabrication of thin colloidal films involved the immersion and withdrawal (with constant velocity) by a specially built withdrawal apparatus (see figure 5.1) in and out of a bath containing the dispersed colloidal carbon and silica in an acetone and water solvent mixture. Varying the withdrawal velocity, acetone volume fraction and number of immersions (i.e. withdrawals) determined the resulting film thickness.

To prepare the colloidal bath, aqueous dispersions of silica and of

carbon were mixed with acetone. Methanol has been used previously but acetone was preferred because:

- (i) acetone is far less toxic than methanol
- (ii) the acetone based baths appeared to be stable for longer periods of time than the methanol based baths.

FIGURE 5.1 WITHDRAWAL APPARATUS



Some difficulty was experienced in the attempts to produce aqueous colloidal carbon dispersions. To disperse colloidal carbon in water a surfactant was required (see reference 50). The concentration of the carbon

needed to be (approximately) more than 10% (w/w) because when too much water was present in the mixed carbon, silica, water and acetone bath the produced coating was found to be uneven due to the slow evaporation of the solvents, resulting in the "settling" of the colloids (see figure 5.1). In other words, very fast evaporation rates of the solvents gave the best film uniformity.

Several surfactants were tried:

(i) from I.C.I. Aust. Pty. Ltd.: Tween 20, Tween 60, Tween 80, Teric N8, Teric N20, Teric N30, Teric N40, Teric N100, Alkanate 3SN5 and Alkanate 3SL3.

(ii) from Albright and Wilsons Pty. Ltd.: Epimin SQ25 and Epigen BB-Au.

(iii) from Rohm and Haas Pty. Ltd.: Orotan 731 (or Tamol NNO).

5.2.1 CLEANING PROCEDURES.

Of these surfactants, Teric N30 seemed to be the best surfactant to disperse colloidal carbon (Degussa Special Black 4) and hence avoid coagulation or gelling when mixed with aqueous colloidal silica and acetone. Although FW200 carbon black could be dispersed in water, none of these aqueous dispersions remained stable in the mixed colloidal silica and acetone bath.

The production of the aqueous colloidal carbon dispersions involved two hours of grinding the dispersion, using a ball mill. The most stable dispersion consisted of:

Degussa Special Black 4	 8.0 g	(20% w/w)
I.C.I. Teric N30	 1.6 g	(4% w/w)
Doubly Distilled Water	 32.0 ml	

After ball mill grinding the sol was then ultrasonicated for 15 minutes

prior to experimental use.

It was also observed that outside the range of carbon to silica weight ratios of 1:2 to 3:1 the mixed colloidal silica and carbon (in water and acetone) baths would not remain stable for more than one day.

Spraying aqueous dispersions of mixed colloidal carbon and silica onto the substrate is another method for producing thin film coatings. For the large scale manufacture of photothermal solar selective surfaces this method would be the most economical and safest, in fact Degussa have fabricated coatings this way, but unfortunately we did not have the resources to attempt this.

5.2 EXPERIMENTAL CHARACTERISATION OF THE COATINGS.

5.2.1 CLEANING PROCEDURES.

"Sail brand (China) No.23" microscope glass slides were used in all (photothermal selective surface) optical measurements (except for calibration purposes, see section 5.2.4) and the cleaning of the glass slides involved the scrubbing with paper towels saturated with Decon 90 (obtained from Selby Scientific Aust. Pty. Ltd.) To remove the excess Decon 90 from the glass surface, the slides were immersed in doubly distilled water for approximately 5 minutes with agitation or at least 20 minutes without agitation. This immersion procedure was usually repeated six to eight times. The clean glass slides were then stored in dessicators (containing "silica gel" to ensure a dry atmosphere) until required for coating purposes, usually one to three days later.

5.2.2 COPPER COATINGS.

Coating the glass slides with copper could be achieved by either

vacuum evaporation (using an "Airco Temescal, electron beam evaporator (Berkley California)") or by electroless metal deposition.

The most convenient procedure for plating the clean glass slides using the electroless method involved the immersion of the glass slides for approximately one minute in a bath containing:

Stannous Chloride	5.0 g
Hydrochloric Acid (37%)	10.0 ml
Doubly Distilled Water	1000 ml

After subsequent rinsing with doubly distilled water the slides were then immersed for approximately one minute in a bath containing:

Palladium Chloride	0.1 g
Hydrochloric Acid (37%)	0.1 ml
Doubly Distilled Water	1000 ml

Again, after subsequent rinsing with doubly distilled water the slides (now "activated") were then immediately immersed into a "plating" bath which contained:

Sodium hydroxide	3.0 g
Sodium potassium tartrate	12.0 g
Copper Sulphate	3.0 g
Formalin	3.0 ml
Doubly Distilled Water	297 ml

Almost instantaneously the glass slides were coated with a semi-transparent black film which then progressed, with time, to appear

metallic and (copper) orange in colour. The coated slides were then removed from the bath after approximately 50 seconds. If kept in longer the copper film would then "blister" due to the formation of trapped hydrogen gas. The produced film (50 seconds immersion time) had an emissivity of 0.023 (at 50°C) and hence could be used as a part of a photothermal solar selective surface. Unfortunately it was observed that unless all traces of grease were removed from the glass surface, "patchy" copper films would result. Difficulty was experienced in continuously producing clean glass slides, clean enough for electroless copper plating.

For practical ease and optical consistency, all copper coatings, on glass, were produced by vacuum evaporation. The thickness of the films were typically 150 nm.

5.2.3 COLLOIDAL COATINGS

The clean glass slides and copper coated slides were coated with the mixed colloidal carbon and silica by dipping the slides into baths containing colloidal carbon, colloidal silica, acetone and water. (see section 5.1) The thickness of the film (as mentioned in section 5.1) was determined by the withdrawal rate, concentration of acetone and the number of immersions.

It was assumed that the ratios of carbon to silica in the coatings were the same as the ratios produced in the baths. Attempts were made to verify this by electron beam microanalysis but this was unsuccessful because the coatings were too thin (for their low density). The conditions for preparing these colloidal coatings are presented in table 5.1.

5.2.4 REFLECTANCE AND TRANSMITTANCE

Total and diffuse reflectances of the coated glass slides (as a function of wavelength) were measured on a Beckmann DK2A spectrophotometer using Halon G80 (powdered teflon /164/) as the reflectance reference. Calibrations with Schott B270 glass /182/ slides and vacuum evaporated copper coated glass slides gave absolute total reflectances. Absolute diffuse reflectance values were obtained from calibrations with the Halon G80 reference (see table 5.2).

Transmittance values of the coated slides were measured on a Hitachi EPS 3T spectrophotometer. Calibration with B270 glass gave the absolute transmittance values.

The repeated measurement of transmittance and reflectance of some selected samples gave an indication of the errors of these measurements. The majority of the deviations from the average measurement were within 2% of this value, in some cases up to 5%. Unfortunately these errors do not give information about the accuracy of the values. One only has to observe the "jumps" or discontinuities of the reflectance vs. wavelength and transmittance vs. wavelength at 700 nm - the changeover of detectors. This discrepancy is probably due to the poor signal to noise ratio and possible non linearity of the lead sulphide detector at and below 800 nm, resulting in misleading calibrated values. For the purpose of diagrammatical clarity the error bars of reflectance and transmittance values are not included in the majority of the graphs presented.

5.2.5 ABSORPTANCE AND THERMAL EMITTANCE

Solar absorptance values were calculated from measurements made on an

absorptometer (using a tungsten lamp as the representation of the solar spectrum) and using vacuum evaporated copper as the reference, and the equation:

$$a_s = 1.0 - 0.90 (R_{as}/R_{ao}) \quad (5.1)$$

where R_{as} and R_{ao} were the (zeroed) voltage readouts of the coated sample and copper reference respectively, and the values obtained gave the solar absorptance.

The thermal emittance values were calculated from measurements on a Rotating Oven Emittance of the Gier-Dunkle type using vacuum evaporated copper as the reference, and the equation:

$$e_t = 1.0 - 0.98 (R_{es}/R_{eo}) \quad (5.2)$$

where R_{es} and R_{eo} were the (zeroed) voltage readouts of the coated sample and the copper reference respectively. The values obtained gave the thermal emittances of the surfaces at 50°C.

Measurements were done in duplicate and the averages were assumed to be the correct values. Errors of up to 2% of the values were observed.

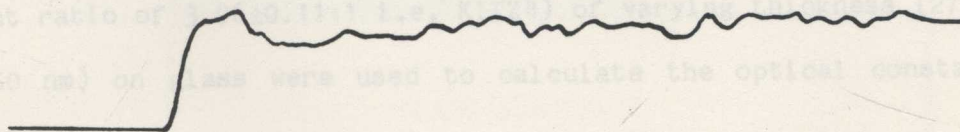
5.2.6 FILM THICKNESS

The thickness of the films were obtained by calculations of measurements done on a "Rank Taylor-Hobson Talystep". The printouts (see figure 5.2) gave a scaled "picture" of the surface. The film thickness was determined by the average of approximately 20 measurements of the surface printout, where the statistical mean was taken to be the experimental

error.

FIGURE 5.2 TRACING OF THE TYPICAL PRINTOUTS USED FOR FILM THICKNESS

DETERMINATION (KITZ4)



5.2.7 DENSITIES

The densities of the coatings (deposited on "Mediglass" cover slips) were obtained by measuring the mass on a "Sartorius 2405" balance and dividing this value by its volume. The volume was determined by calculating the surface area and thickness (on the Talystep) of the coating. To reduce the errors of the mass measurements, lightweight glass slides were used. As a result revised cleaning procedures were required because of the fragility of these slides. Cleaning the glass slides involved immersion for 24 hours in a water solution containing 5% (v/v) Decon 90 then subsequent repeated rinsings (approximately 6 rinsings in doubly distilled water).

5.3 OPTICAL CHARACTERISATION OF THE MIXED COLLOIDAL CARBON AND SILICA COATING

The optical constants of a homogeneous absorbing medium (i.e. n , the refractive index, and k , the extinction coefficient) can be calculated from

reflectance and transmittance measurements of the medium of known thickness on a non-absorbing substrate (e.g. glass) /165/.

5.3.1 EXPERIMENTAL DETERMINATION OF n AND k .

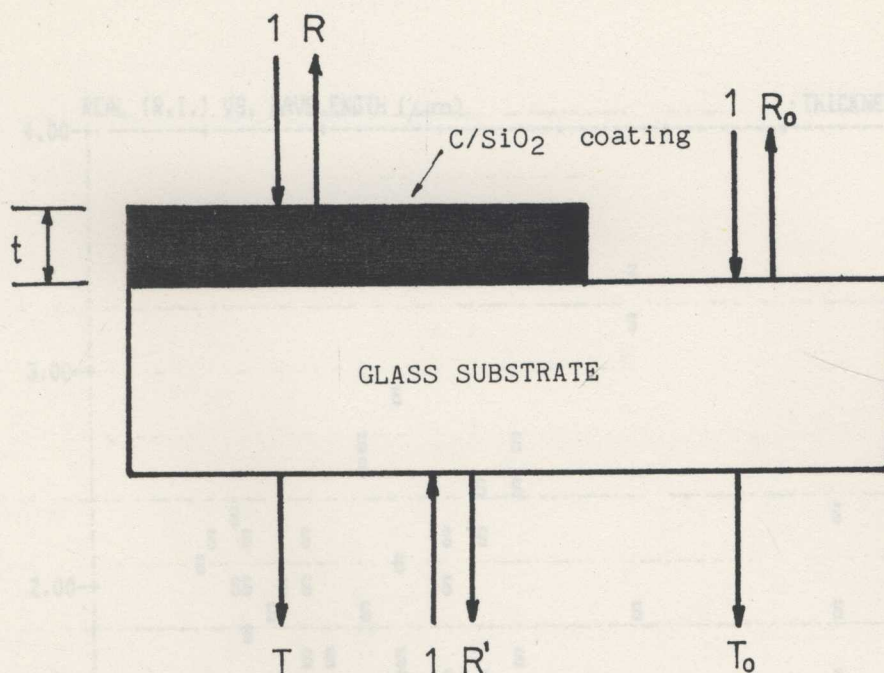
Two mixed colloidal carbon and silica coatings (with a carbon to silica weight ratio of $3.06 \pm 0.11:1$ i.e. KITZ4) of varying thickness (270 ± 30 nm and 515 ± 50 nm) on glass were used to calculate the optical constants of the coating medium.

To calculate n and k of the absorbing medium, the reflectance and transmittance measurements (as a function of wavelength) of the colloidal coating on top of the glass, reverse side of the coated glass and of the glass substrate are required (see figure 5.3). This data yields (using the Bivariate method from reference 165) a set of values that correspond to the air/medium reflectances, R , substrate/medium reflectances, R' , and transmittances, T , of the medium (see table 5.3 and graphs 5.1 and 5.2).

Further calculations involving R , T , t and R' , T , t yield various n and k values, where possible solution sets must have continuous variation of n with wavelength. Also the n and k values obtained from using R in the calculations and those from using R' (denoted by S in figures 5.4 and 5.5) must overlap (denoted by # in figures 5.4 and 5.5) or be in close proximity (see figures 5.4 and 5.5). Varying the value of t (film thickness) will also vary n and k . This is done to account for the experimental error of t and as a result also gives an indication of the error in n and k .

Once the n and k values are found from calculations involving the Bivariate method they can then be compared with the n and k values calculated from the Maxwell Garnett theory.

FIGURE 5.3 EXPERIMENTAL MEASUREMENTS USED TO DETERMINE n AND k OF THE COATINGS



T_0 = Transmittance through glass substrate
 R_0 = Reflectance of glass substrate
 t = Film thickness
 R = Front reflectance
 T = Transmittance through coating
 R' = Back reflectance

Note that this determination (i.e. Bivariate method) requires that:

- (i) the film is uniformly thick (parallel sided).
- (ii) the film is smooth (this sort of error tends to increase the apparent absorption and hence k).
- (iii) the film is homogeneous from top to bottom i.e. no grading.

5.3.2 THEORETICAL DETERMINATION OF n AND k .

Once the n and k values are found from calculations involving the Bivariate method they can then be compared with the n and k values calculated from the Maxwell Garnett theory.

FIGURE 5.4 BIVARIATE n AS A FUNCTION OF WAVELENGTH (KITZ4-5 AS AN EXAMPLE)

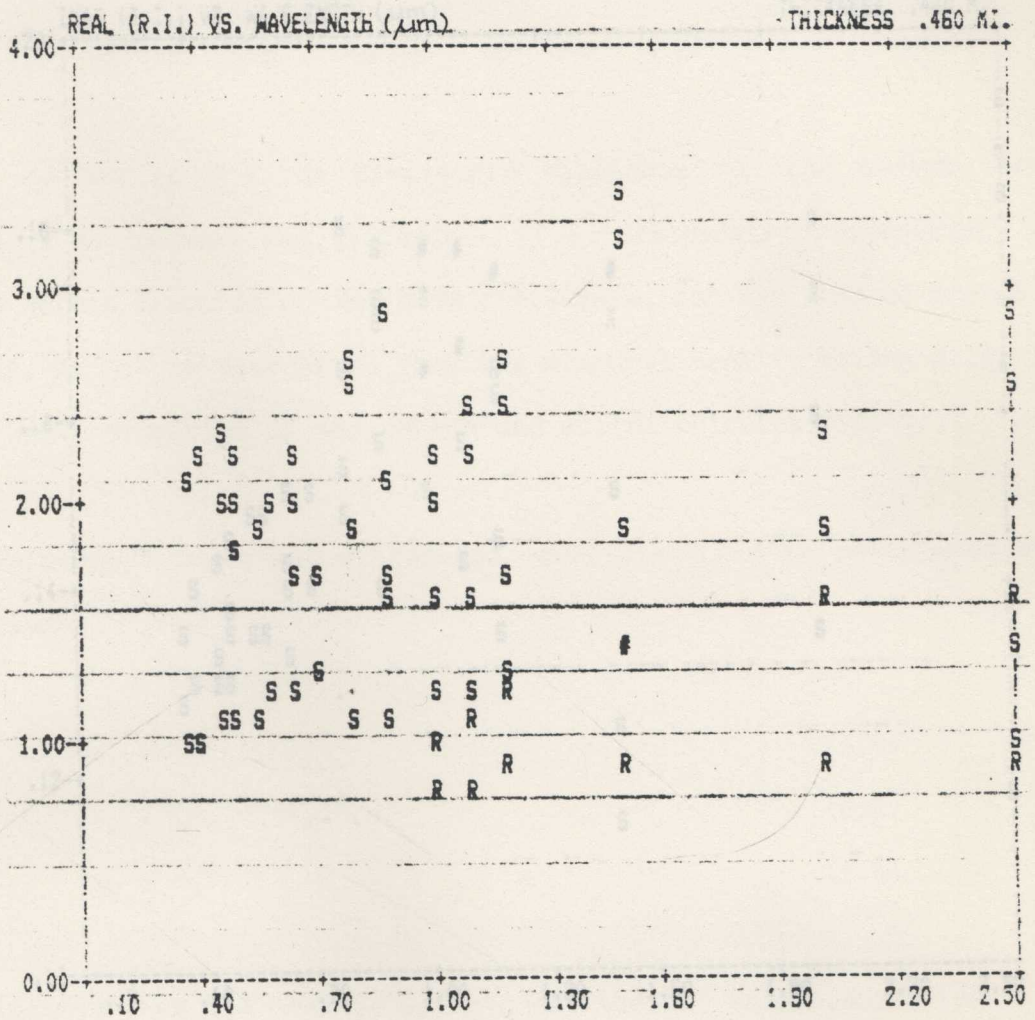
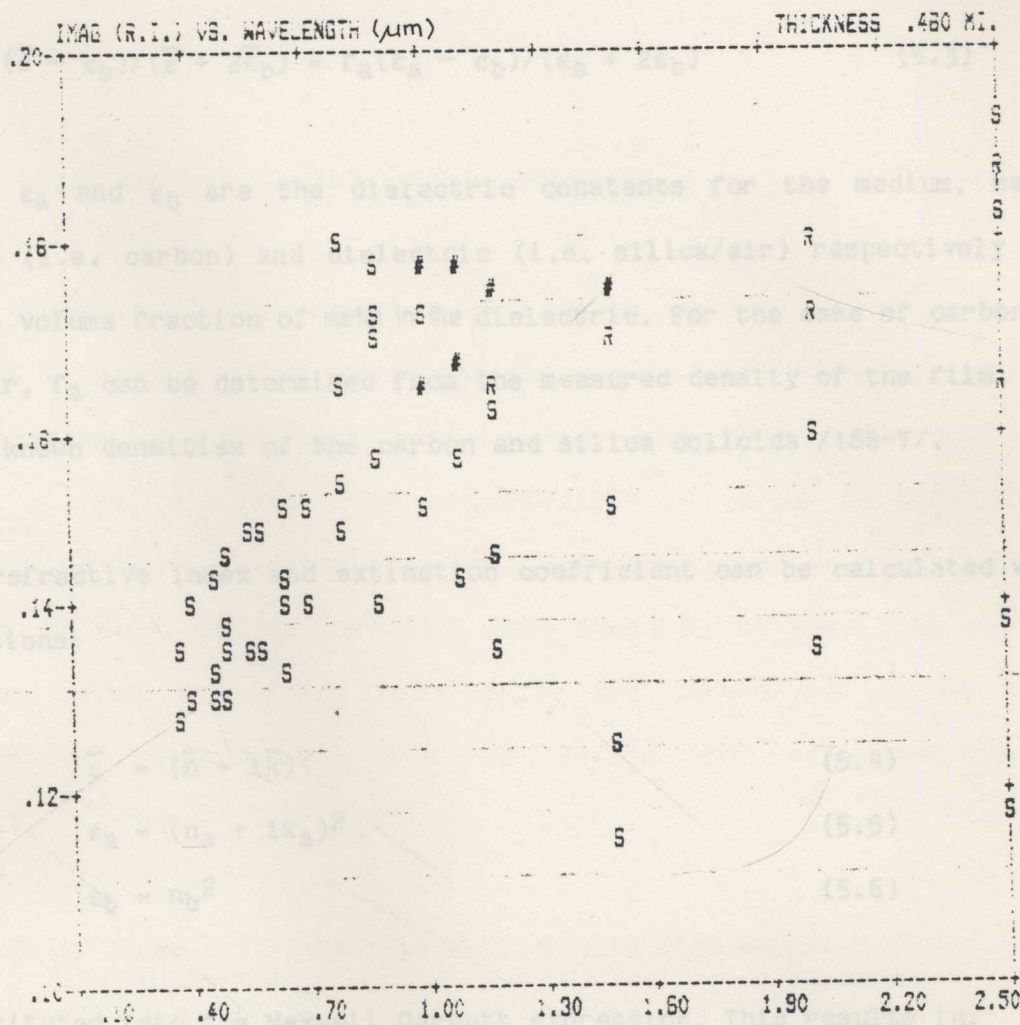


FIGURE 5.5 BIVARIATE k AS A FUNCTION OF WAVELENGTH (KITZ4-5 AS AN EXAMPLE)



$$k^2 = \frac{(n_0^2 - n_d^2)(1 + 2f_d) + 2n_0^2(1 - f_d)}{(n_0^2 + n_d^2)} \quad (5.7)$$

$$2nk = \frac{(n_0^2 - n_d^2)(1 + 2f_d) + 2n_0^2(1 - f_d)}{(n_0^2 + n_d^2)} \quad (5.8)$$

$$a = (n_0^2 - n_d^2)(1 + 2f_d) + 2n_0^2(1 - f_d) \quad (5.9)$$

$$b = 2n_0n_d(1 + 2f_d) \quad (5.10)$$

$$c = (n_0^2 - n_d^2)(1 - f_d) + n_0^2(2 + f_d) \quad (5.11)$$

$$d = 2n_0n_d(1 - f_d) \quad (5.12)$$

To determine n and k of the medium the n values of fused silica (132/

5.3.2a THE MAXWELL GARNETT EQUATION

As shown in section 4 the Maxwell Garnett equation is:

$$(\bar{\epsilon} - \epsilon_b)/(\bar{\epsilon} + 2\epsilon_b) = f_a(\epsilon_a - \epsilon_b)/(\epsilon_a + 2\epsilon_b) \quad (5.3)$$

where $\bar{\epsilon}$, ϵ_a and ϵ_b are the dielectric constants for the medium, metal particles (i.e. carbon) and dielectric (i.e. silica/air) respectively and f_a is the volume fraction of metal in the dielectric. For the case of carbon in silica/air, f_a can be determined from the measured density of the film, and with the known densities of the carbon and silica colloids /166-7/.

The refractive index and extinction coefficient can be calculated when the relations:

$$\bar{\epsilon} = (\bar{n} + i\bar{k})^2 \quad (5.4)$$

$$\epsilon_a = (n_a + ik_a)^2 \quad (5.5)$$

$$\epsilon_b = n_b^2 \quad (5.6)$$

are substituted into the Maxwell Garnett expression. This results in:

$$\bar{n}^2 - \bar{k}^2 = (ab + cd)/(c^2 + d^2) \quad (5.7)$$

and $2\bar{n}\bar{k} = (bc - ad)/(c^2 + d^2) \quad (5.8)$

where $a = (n_a^2 - k_a^2)(1 + 2f_a) + 2n_b^2(1 - f_a) \quad (5.9)$

$$b = 2n_ak_a(1 + 2f_a) \quad (5.10)$$

$$c = (n_a^2 - k_a^2)(1 - f_a) + n_b^2(2 + f_a) \quad (5.11)$$

$$d = 2n_ak_a(1 - f_a) \quad (5.12)$$

To determine n and k of the medium the n values of (fused) silica /182/

in air are first calculated using the Maxwell Garnett treatment. Once these values of n are known (i.e. n_b), the optical constants of amorphous and amorphous hydrogenated carbon /168-9/ (i.e. n_a and k_a) are substituted into equations 5.7 and 5.8 to yield n and k of the medium (see tables 5.4 and 5.5 and graphs 5.3 to 5.6).

5.3.2b SOLAR ABSORPTANCE AND THERMAL EMITTANCE

The Maxwell Garnett equation was tested to see if it gave good agreement with the n and k values deduced experimentally. It should be noted that the Maxwell Garnett formula is in many cases not strictly applicable in view of the relatively high concentration of carbon in many of the coatings, and in view of the fact that some scattering of light had been observed. However, if the agreement were found to be good, the equation would be useful in helping to optimise the carbon and silica volume fractions for high normal solar absorptance and low normal thermal emittance.

It can be shown /157/ that the reflectivity from any film of thickness, t , and refractive index, $\bar{n} + i\bar{k}$, on a substrate of refractive index, $n_0 + ik_0$, is:

$$R(\lambda) = \frac{(g^2 + h^2)\exp(\bar{\alpha}) + (l^2 + m^2) + A\cos(\bar{\gamma}) + B\sin(\bar{\gamma})}{\exp(\bar{\alpha}) + (g^2 + h^2)(l^2 + m^2)\exp(-\bar{\alpha}) + C\cos(\bar{\gamma}) + D\sin(\bar{\gamma})} \quad (5.13)$$

$$\text{where } A = 2(gl + hm) \quad (5.14)$$

$$B = 2(gm - lh) \quad (5.15)$$

$$C = 2(gm - hm) \quad (5.16)$$

$$D = 2(gm + lh) \quad (5.17)$$

where $H(\lambda)$ is the spectral solar irradiance expressed in W.m^{-2} and $\alpha(\lambda)$ is

with $g = \frac{1 - \bar{n}^2 - \bar{k}^2}{(1 + \bar{n})^2 + \bar{k}^2}$ (5.18)

$h = \frac{2\bar{k}}{(1 + \bar{n})^2 + \bar{k}^2}$ (5.19)

$1 = \frac{\bar{n}^2 - n_0^2 + \bar{k}^2 - k_0^2}{(\bar{n} + n_0)^2 + (\bar{k} + k_0)^2}$ (5.20)

$m = \frac{2(\bar{n}k_0 - n_0\bar{k})}{(\bar{n} + n_0)^2 + (\bar{k} + k_0)^2}$ (5.21)

and $\bar{\alpha} = (4\pi\bar{k}t)/\lambda$ (5.22)

$\bar{\gamma} = (4\pi\bar{n}t)/\lambda$ (5.23)

From a simplification of Kirchhoff's law for an opaque surface the relations between normal reflectivity, normal solar absorptance and normal thermal emittance is given by:

$a(\lambda) = 1 - R(\lambda)$ (5.24)

$e(\lambda, T) = 1 - R(\lambda, T)$ (5.25)

$\approx 1 - R(\lambda)$ (5.26)

The normal solar absorptance is defined by the integration over wavelength /11,12/:

$a_s = \frac{\int_0^\infty a(\lambda)H(\lambda) d\lambda}{\int_0^\infty H(\lambda) d\lambda}$ (5.26)

where $H(\lambda)$ is the spectral solar irradiance expressed in W.m^{-2} and $a(\lambda)$ is

given by equation 5.24.

The normal thermal emittance is similarly defined as:

$$e_t = \frac{\int_0^\infty e(\lambda, T) e_b(\lambda, T) d\lambda}{\int_0^\infty e_b(\lambda, T) d\lambda} \quad (5.27)$$

with
$$e_b(\lambda, T) = C_1 / (\lambda^5 [\exp(C_2 / \lambda T) - 1]) \quad (5.28)$$

where λ is the wavelength expressed in metres, T is the temperature, $C_1 = 1.19 \times 10^{-16} \text{ W.m}^{-2}$, $C_2 = 1.4388 \times 10^{-2} \text{ m.K}$ and $e(\lambda, T)$ is given by equation 5.25.

By calculating the various $\bar{n}$ and $\bar{k}$ values from the Maxwell Garnett formula for various volume fractions (f_a) of carbon and silica (assuming a packing density of approximately 0.5) and substituting these values into equation 5.13 then various values of a_s and e_t can be obtained. The equation for the thermal efficiency, a_m , (effective absorption efficiency) of the solar selective surface /11,12,157/ can then be used to calculate the optimum combination of a_s and e_t . The thermal efficiency equation is:

$$a_m = a_s - (e_t \sigma T^4) / G \quad (5.29)$$

where $\sigma = 5.6693 \times 10^{-8} \text{ W.m}^{-2}.\text{K}^{-4}$ and is known as the Stefan-Boltzman constant, T is the temperature of the surface and G is the incident solar irradiance (taken to be approximately 1000 W.m^{-2}).

5.3.3 DISCUSSION OF RESULTS FOR n AND k .

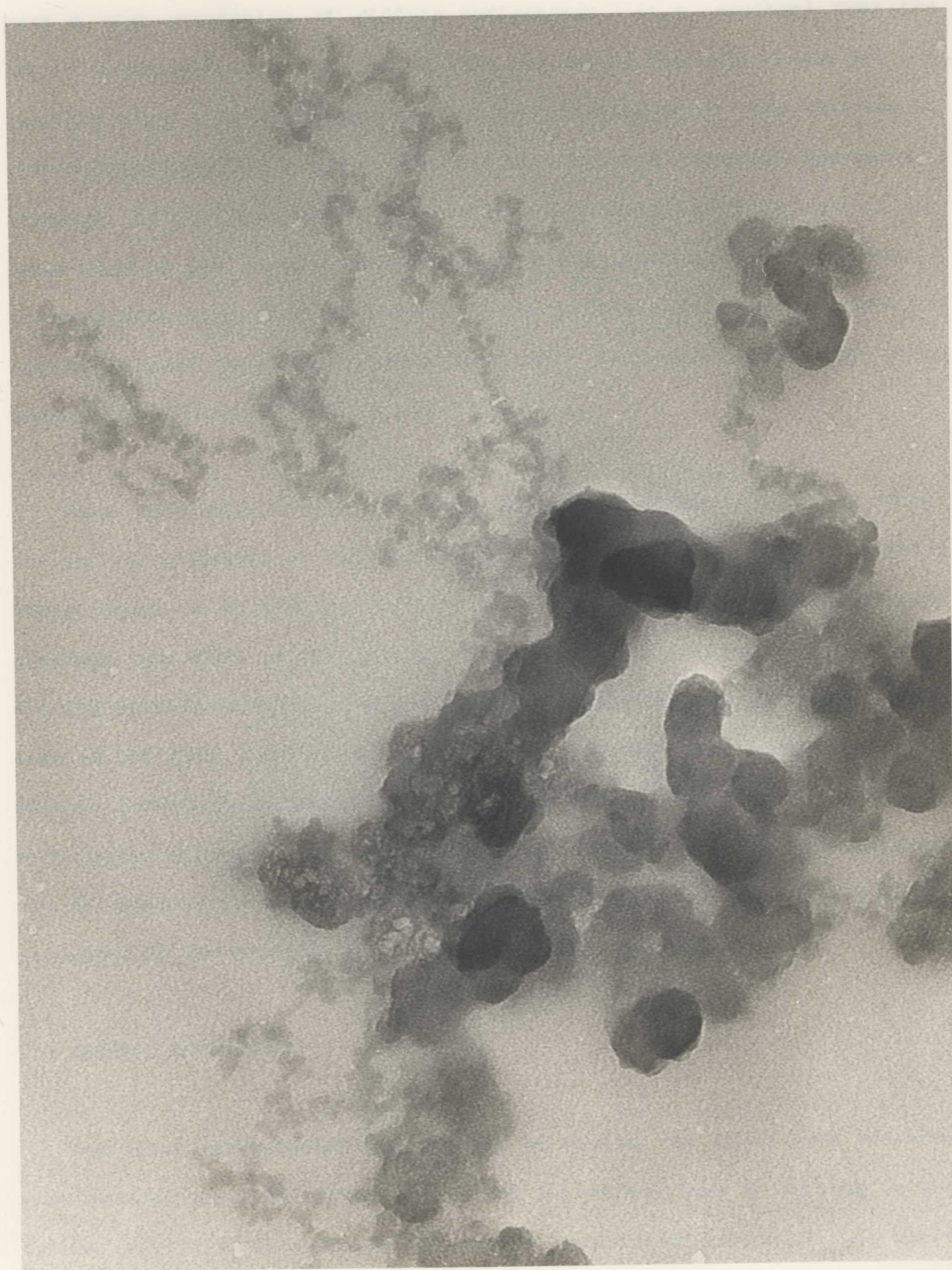
Unfortunately, poor agreement between the n and k values obtained from

the Bivariate calculations involving R and R' was observed. Furthermore, a large number of possible solutions were obtained. Consequently, the n values that were in the physically reasonable range of 1.00 and 1.60 and which were continuous with respect to wavelength were chosen as the correct solutions and were compared to the Maxwell Garnett results (graphs 5.5 and 5.6) and were in agreement within the large experimental errors. From the n values chosen, from the Bivariate method, the corresponding k values were then obtained. The deviation of the n values was large and the validity of these values is questionable. The deviation of the k values, however, was not so significant but the maximum k values were far below the k values obtained from the Maxwell Garnett equation.

One reason for the discrepancy, apart from the general inapplicability of the Maxwell Garnett formula, could be the use of amorphous carbon optical constants. The Degussa company have analysed their carbon and labelled it "semi-graphitic". The optical constants of graphite /170/ are larger than those for amorphous carbon, especially the k values. The use of graphite optical constants increases the calculated k values but this would increase the calculated values even more. For comparison Maxwell Garnett calculations involving hydrogenated carbon were also done, but those results have also shown significant differences from the results obtained by the Bivariate method (see graph 5.6).

The clustering of carbon and silica in the colloidal film may be the reason for these discrepancies. An electron microscopy study of the film (see figure 5.6) has shown the dipped coating to consist of islands of colloidal silica and islands of colloidal carbon. This clustering of carbon makes the Maxwell Garnett treatment invalid because the theory requires that the carbon colloids are spaced far apart from each other (see section 4.1). Measurements of the total and diffuse reflectances of the colloidal

FIGURE 5.6 CARBON/SILICA /185/



50 nm

coatings (see graph 5.7, being a typical example of all the coatings) support the electron microscopy studies because they show that the films have a high proportion of diffuse reflectance (i.e. scatter) over the entire wavelength range (360 nm to 2500 nm), where the only trends are the expected lower intensities of the diffuse reflectances at long wavelengths with decreasing film thickness (because the degree of roughness decreases). Although, it was expected to observe some scattering of light due to the large size of the carbon colloids (ideally one would wish to use particle sizes approximately 5 nm in diameter - see section 4.1.1c) the expectation was for a peak in diffuse reflectance at a particular wavelength with negligible diffuse reflectance elsewhere.

Water absorption of the film (from atmospheric water vapour) may change the optical constants of the Maxwell Garnett calculations, but the expected change would be an increase in both n and k . Therefore, the discrepancies observed are most likely due to the failure to fabricate a dispersed coating because both theories are based on highly dispersed films. Should this be the case, then it seems plausible to predict that according to the Maxwell Garnett calculations (based on amorphous carbon and fused silica) much higher effective solar absorptance efficiencies than already achieved may be obtained if the mixed colloidal carbon and silica were more evenly dispersed in the coatings and if smaller particles could be used.

5.4 THERMAL EFFICIENCY

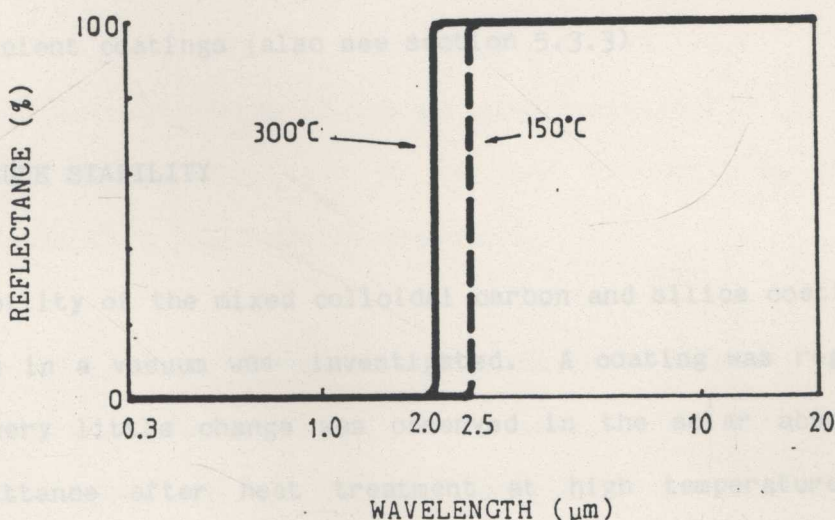
The solar absorptances and thermal emittances (at 50°C) were measured from several mixed colloidal carbon and silica coatings of varying weight ratios and film thicknesses on vacuum evaporated copper. For these coatings, the effective absorptance efficiencies, a_m , (see equation 5.29) were calculated (see table 5.7 and graph 5.8).

From the results it can be concluded that the most efficient solar selective surface contains a 1:1 carbon to silica weight ratio with a film thickness between 350 nm to 400 nm.

5.5 REFLECTANCES OF THE PHOTOTHERMAL SURFACES

Total and diffuse reflectances of the colloidal carbon and silica coatings on copper were measured so as to compare the reflectance dependence on wavelength of the coatings with the "ideal" photothermal solar selective surface [11,12] (see figure 5.7).

FIGURE 5.7 SPECTRAL PROFILE OF AN "IDEAL" PHOTOTHERMAL SURFACE



The total and diffuse reflectance results (see tables 5.8 and graphs 5.9) show that the absorbing efficiency of the thinner films could be enhanced (and approach the spectral profile of the ideal surface) if the diffuse reflectances (i.e. scatter of the incident light) could be reduced. A possible method of reducing the diffuse reflectances would be to fabricate a highly dispersed film. The thinner films were chosen because the high

diffuse reflectance of these films occurs near the visible region, where a high reflectance is undesirable, while the thicker films have high diffuse reflectances at longer wavelengths, where the high reflectance is required. This is a commonly observed phenomenon in other types of film growth where the scale size of the roughness of the surface increases with film thickness. The plot of the specular reflectance (i.e. difference between the diffuse and total reflectances) of sample KITZ1-2 (see graph 5.10) is an example of the predicted higher absorbing efficiency if the diffuse reflectances could be minimised because it shows the approach of the spectral profile to the "ideal" profile.

Although no obvious trend was observed from graphs 5.9 concerning the carbon to silica ratio, it can be hypothesised that the fabrication of mixed colloidal carbon and silica films that are more dispersed may result in more efficient coatings (also see section 5.3.3).

5.6 TEMPERATURE STABILITY

The stability of the mixed colloidal carbon and silica coatings at high temperatures in a vacuum was investigated. A coating was regarded as stable if very little change was observed in the solar absorptance and thermal emittance after heat treatment at high temperatures for long periods of time.

The results compare well with previous studies /161/ and are presented on the next page.

One can conclude from these and previous results /161/ that the mixed colloidal carbon and silica coating is a promising candidate for use as a high temperature photothermal solar selective surface.

EXPOSURE		$a_s(\%)$	$e_t(50^\circ\text{C})(\%)$	THICKNESS	
TEMPERATURE	PERIOD	APPROXIMATION OF		(nm)	
($^\circ\text{C}$)	(HOURS)	$C : \text{SiO}_2$			
VERB2-1	NIL	NIL	84.9 ± 0.1	4.9 ± 0.1	360 ± 60
VERB2-4	NIL	NIL	93.0 ± 0.2	13.2 ± 0.1	610 ± 70
VERB2-1	400	100	85.6 ± 0.4	5.3 ± 0.1	310 ± 60
VERB2-4	400	100	93.3 ± 0.4	14.4 ± 0.2	590 ± 50
VERB2-1	500	100	86.5 ± 0.4	5.4 ± 0.2	335 ± 30
VERB2-4	500	100	94.0 ± 0.7	14.5 ± 0.4	630 ± 50
VERB2-1	500	300	86.3 ± 2.5	5.3 ± 0.1	*
VERB2-4	500	300	91.6 ± 2.5	14.1 ± 0.2	*

#There was no apparent change in the abrasion resistance.

*The glass slides "buckled" due to the heat treatment. As a result the thickness of the film could not be measured.

A colloidal carbon and silica coating was exposed to air at a temperature of 150°C for 50 hours. The coating became more adherent with no noticable change in the solar absorptance or thermal emittance. Unfortunately much longer exposures to air at temperatures around 150°C resulted in the oxidation of the copper substrate. This destroys the efficient thermal conversion of the coatings by drastically reducing the infrared reflectivity of the substrate.

One can conclude from these and previous results /161/ that the mixed colloidal carbon and silica coating is a promising candidate for use as a high temperature photothermal solar selective surface.

TABLE 5.1a

CARBON TO SILICA RATIOS (w/w)		
SAMPLE	C : SiO ₂	APPROXIMATION OF C : SiO ₂
VERB1	1 : (2.21±0.07)	1 : 2
VERB2	1 : (0.98±0.05)	1 : 1
VERB3	2 : (0.98±0.08)	2 : 1
VERB4	5 : (3.92±0.23)	5 : 4
KITZ1	1 : (2.21±0.07)	1 : 2
KITZ2	1 : (0.98±0.05)	1 : 1
KITZ3	2 : (0.98±0.08)	2 : 1
KITZ4	3 : (0.98±0.11)	3 : 1

TABLE 5.1b

BATH CONCENTRATIONS			
(Approximate volumes (mls) of)			
BATH	CARBON SOL	SILICA SOL	ACETONE
A	3.2	4.8	40
B	3.2	4.8	80
C	4.8	3.2	40
D	4.8	3.2	120
E	6.0	2.0	40
F	6.0	2.0	160
G	5.2	2.8	40
H	5.2	2.8	400
I	1.6	2.4	100
J	2.4	1.6	100
K	3.0	1.0	100
L	3.3	0.7	100

TABLE 5.1c (cont.)

PRODUCTION PARAMETERS OF THE MIXED CARBON AND SILICA COATINGS

WITHDRAWAL RATE = 5.0 mm/s
(AT ROOM TEMPERATURE)

SAMPLE	No. OF WITHDRAWALS	BATH CONC.	FILM THICKNESS (nm)
VERB1 - 1	4	A	360±20
- 2	4	A	400±20
	1	B	
- 3	4	A	420±30
	1	B	
- 4	4	A	430±40
	2	B	
- 5	5	A	500±20
- 6	5	A	580±30
	1	B	
- 7	6	A	710±30
VERB2 - 1	1	C	360±60
	1	D	
- 2	1	C	430±70
	2	D	
- 3	2	C	490±60
- 4	2	C	610±70
	1	D	
- 5	3	C	630±60
VERB3 - 1	1	E	260±60
- 2	1	E	300±60
	1	F	
- 3	1	E	370±70
	2	F	
- 4	1	E	430±90
	3	F	
- 5	2	E	430±70
- 6	3	E	560±90
VERB4 - 1	3	H	140±40
- 2	1	G	250±50
- 3	1	G	330±50
	4	H	
- 4	1	G	380±50
	7	H	
- 5	1	G	390±50
	9	H	
- 6	2	G	520±70
- 7	2	G	550±50
	2	H	
- 8	2	G	610±30
	4	H	

TABLE 5.1c (cont.)

SAMPLE	No. OF WITHDRAWALS	BATH CONC.	FILM THICKNESS
KITZ1 - 1	2	I	46±7
- 2	4	I	83±10
- 3	7	I	150±30
- 4	10	I	230±40
- 5	14	I	320±60
KITZ2 - 1	2	J	104±18
- 2	4	J	190±20
- 3	6	J	220±60
- 4	8	J	340±60
- 5	10	J	410±80
KITZ3 - 1	1	K	73±14
- 2	3	K	210±40
- 3	4	K	280±80
- 4	5	K	360±90
- 5	6	K	380±130
KITZ4 - 1	3	L	270±30
- 2	4	L	430±70
- 3	5	L	490±50
- 4	6	L	500±40
- 5	7	L	510±50

TABLE 5.2

REFLECTANCES OF STANDARDS USED (%)

WAVELENGTH (nm)	SCHOTT B270	COPPER	POWDERED TEFLON
360	9.3179	41.5	99.0
400	9.0858	47.5	99.3
450	8.8912	55.2	99.3
500	8.7579	60.0	99.4
550	8.6613	66.9	99.4
600	8.5884	93.3	99.4
650	8.5314	96.6	99.4
700	8.4855	97.5	99.4
800	8.4153	98.1	99.4
900	8.3629	98.4	99.4
1000	8.3208	98.5	99.4
1100	8.2847	98.5	99.4
1200	8.2521	98.5	99.3
1500	8.1633	98.5	99.2
2000	8.0122	98.6	98.1
2500	7.8369	98.6	96.0

REFLECTANCES OF KITZ4 - 1 AND KITZ4 - 5 COATINGS

WAVELENGTH (nm)	OF COATINGS ON GLASS									OF THE COATINGS					
	SPECULAR REFLECTANCE (%)					TRANSMITTANCE (%)				REFLECTANCE (%)				TRANSMITTANCE (%)	
	FRONT		BACK		GLASS			GLASS		FRONT		BACK			
	-1	-5	-1	-5		-1	-5			-1	-5	-1	-5	-1	-5
360	2.41	0.08	7.77	8.46	9.13	55.3	10.2	90.5		0.79	0.02	3.30	4.06	58.2	10.7
400	2.63	0.10	7.13	7.91	8.98	58.2	12.0	91.2		0.82	0.03	2.67	3.52	60.9	12.7
450	2.93	0.15	6.42	7.21	8.61	61.2	14.6	91.1		1.08	0.05	2.10	2.97	64.2	15.3
500	3.35	0.21	5.91	6.79	8.33	63.9	17.2	91.2		1.40	0.07	1.70	2.67	67.1	18.1
550	3.73	0.30	5.48	6.44	8.22	66.3	19.8	91.3		1.66	0.12	1.29	2.35	69.6	20.8
600	4.07	0.39	5.17	6.21	8.11	68.4	22.1	91.5		1.91	0.16	1.02	2.16	71.7	23.2
650	4.42	0.50	4.96	6.02	7.99	70.4	24.4	91.2		2.16	0.23	0.85	2.02	74.1	25.7
700	4.65	0.58	4.75	5.42	7.68	71.8	26.8	90.7		2.38	0.26	0.78	1.53	76.1	28.4
800	5.35	0.84	4.57	6.12	7.98	73.1	24.6	87.5		2.81	0.53	0.39	2.12	80.0	26.9
900	5.43	1.04	4.39	5.81	7.46	74.3	27.9	84.8		2.91	0.69	0.26	2.08	84.1	31.6
1000	5.87	1.44	4.50	5.61	7.42	75.5	30.9	84.5		3.28	1.01	0.42	1.85	85.7	35.1
1100	5.99	1.85	4.49	5.67	7.35	76.5	34.0	84.7		3.36	1.33	0.46	1.98	86.7	38.5
1200	6.23	2.34	4.44	5.59	7.30	77.4	37.1	84.8		3.56	1.73	0.44	1.91	87.6	42.0
1500	6.65	3.84	4.59	5.63	7.23	81.4	45.3	87.4		3.81	2.96	0.77	2.02	89.6	49.8
2000	6.88	6.21	4.82	5.73	7.28	85.8	55.0	90.0		3.79	4.94	1.07	2.11	91.7	58.8
2500	6.83	8.10	5.24	6.00	7.34	90.7	62.6	92.8		3.45	6.58	1.55	2.36	94.1	64.9

TABLE 5.4

OPTICAL CONSTANTS FOR AMORPHOUS CARBON, HYDROGENATED CARBON,
FUSED SILICA AND GRAPHITE

WAVELENGTH (nm)	FUSED SILICA	AMORPHOUS CARBON		HYDROGENATED CARBON		GRAPHITE	
	n	n	k	n	k	n	k
360	1.475	1.98	0.92	1.74	1.30	2.51	1.44
400	1.470	2.07	0.91	1.92	1.23	2.55	1.35
450	1.466	2.17	0.89	2.02	1.12	2.57	1.37
500	1.463	2.27	0.88	2.01	1.02	2.59	1.40
550	1.460	2.36	0.84	2.04	0.92	2.60	1.45
600	1.458	2.41	0.78	1.85	0.90		0.436
650	1.456	2.44	0.72	1.93	0.78		0.442
700	1.455	2.41	0.70	1.99	0.76		0.388
800	1.453	2.31	0.72	2.13	0.58		0.376
900	1.452	2.22	0.81	2.15	0.49		0.290
1000	1.450	2.21	0.97	2.16	0.42		0.247
1100	1.449	2.37	1.16				0.214
1200	1.448	2.55	1.37	2.13	0.30		
1500	1.445	3.20	1.63	2.14	0.20		0.155
2000	1.438	3.73	1.55	2.17	0.10		0.104
2500	1.430	3.65	1.43	2.08	0.09		0.053
2500	1.0229		1.344	0.518		1.143	0.047

VOLUME FRACTIONS OF CARBON AND SILICA USED IN THE
MAXWELL GARNETT CALCULATIONS WERE (FROM KITZ4)

$$C = 18.0 \pm 2.9 \% \text{ (v/v)}$$

$$SiO_2 = 4.8 \pm 0.7 \% \text{ (v/v)}$$

TABLE 5.5

MAXWELL GARNETT OPTICAL CONSTANTS

WAVELENGTH (nm)	FUSED SILICA IN AIR	AMORPHOUS CARBON		HYDROGENATED CARBON	
	n	n	k	n	k
360	1.0250	1.242	0.441	1.312	0.584
400	1.0248	1.244	0.431	1.301	0.550
450	1.0246	1.244	0.416	1.282	0.508
500	1.0245	1.246	0.405	1.262	0.475
550	1.0243	1.243	0.384	1.244	0.436
600	1.0243	1.236	0.357	1.231	0.442
650	1.0242	1.228	0.331	1.212	0.388
700	1.0241	1.226	0.332	1.212	0.376
800	1.0240	1.223	0.340	1.192	0.290
900	1.0240	1.233	0.381	1.181	0.247
1000	1.0239	1.260	0.442	1.174	0.214
1100	1.0238	1.295	0.491		
1200	1.0234	1.328	0.606	1.159	0.155
1500	1.0237	1.353	0.543	1.153	0.104
2000	1.0233	1.337	0.486	1.151	0.053
2500	1.0229	1.344	0.518	1.143	0.047

VOLUME FRACTIONS OF CARBON AND SILICA USED IN THE
MAXWELL GARNETT CALCULATIONS WERE (FROM KITZ4)

$$C = 18.0 \pm 2.5 \% (v/v)$$

$$SiO_2 = 4.8 \pm 0.7 \% (v/v)$$

TABLE 5.6

BIVARIATE OPTICAL CONSTANTS

WAVELENGTH (nm)	KITZ4 - 1				KITZ4 - 5	
	n		k		n	k
360	1.06		.056		1.05	0.12
400	1.06	1.23	.058	.054	1.10	0.12
450	1.10		.058		1.10	0.12
500	1.17	1.19	.057	.055	1.09	0.12
550	1.10	1.22	.057	.053	1.12	0.13
600					1.17	0.13
650					1.22	0.13
700					1.30	0.13
800	1.13	1.25	.047	.043	1.14	0.16
900	1.10	1.37	.048	.036	1.09	0.15
1000	1.10	1.45	.047	.034	1.13	0.15
1100	1.10	1.48	.048	.034	1.16	0.15
1200		1.35 1.50	.047	.033	1.21	0.15
1500	1.13	1.35 1.50	.047	.043 .031	1.36	0.15
2000	1.14	1.37 1.48	.047	.039 .028		
2500		1.35 1.50	.027	.019	1.40	0.16

For the purpose of clarity the errors are not presented in this table but are included in the graphical plots.

Errors of up to 25% of the values were observed.

TABLE 5.7

THERMAL EFFICIENCY

SAMPLE	THICKNESS (nm)	a_s (%)	e_t (%)	a_m (%) (150°C)
VERB1 - 1	360±20	85.7	5.4	75.9
- 2	400±20	84.9	5.2	75.5
- 3	420±30	86.9	6.8	74.6
- 4	430±40	88.5	8.1	73.8
- 5	500±20	90.6	9.9	72.6
- 6	580±30	92.1	11.3	71.6
- 7	710±30	93.1	11.9	71.5
VERB2 - 1	360±60	84.9	4.9	76.0
- 2	430±70	89.1	7.6	75.3
- 3	490±60	90.7	7.5	77.1
- 4	610±70	93.0	13.2	69.0
- 5	630±60	95.6	22.3	55.1
VERB3 - 1	260±60	76.7	3.8	69.8
- 2	300±60	86.6	6.1	75.5
- 3	370±70	87.4	6.6	75.4
- 4	430±90	90.2	9.6	72.8
- 5	430±70	91.7	11.0	71.7
- 6	560±90	94.1	21.6	54.9
VERB4 - 1	140±40	56.8	2.3	52.6
- 2	250±50	84.1	4.6	75.8
- 3	330±50	85.7	6.0	74.8
- 4	380±50	87.8	7.3	74.6
- 5	390±50	89.5	8.4	74.3
- 6	520±70	93.0	14.1	67.4
- 7	550±50	93.0	15.2	65.4
- 8	610±30	94.3	18.2	61.3

Errors of up to 2% of the values were observed.

TOTAL REFLECTANCE (%) ON COPPER

WAVELENGTH (nm)	Cu	KITZ1					KITZ2					KITZ3					KITZ4				
		-1	-2	-3	-4	-5	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5
360	41.5	14.1	10.3	6.2	4.7	3.7	11.6	5.4	3.7	3.1	2.9	17.4	9.6	6.3	4.5	3.8	13.0	7.2	4.8	3.8	3.4
400	47.5	16.7	12.5	7.2	5.4	4.1	13.6	6.3	4.2	3.2	2.8	20.9	11.3	7.3	5.0	4.2	15.0	8.4	5.5	4.2	3.5
450	55.2	21.1	15.6	8.9	6.6	4.7	16.6	8.0	5.0	3.6	3.0	25.9	13.7	9.0	6.0	4.9	18.5	10.2	6.9	5.1	4.0
500	60.0	24.7	18.3	11.1	7.8	5.3	18.9	9.7	5.9	4.1	3.2	29.5	15.9	10.6	7.2	5.6	21.2	11.8	8.4	6.1	4.6
550	66.9	29.5	21.7	13.9	9.8	6.5	27.2	12.0	7.6	4.9	3.5	34.3	19.1	12.9	9.2	6.7	25.4	14.6	10.5	7.8	5.9
600	93.3	47.0	33.4	21.9	15.0	9.5	32.9	18.4	11.6	7.0	4.6	52.3	29.1	19.6	13.1	9.9	40.0	22.1	15.8	11.8	8.7
650	96.6	52.2	37.9	25.1	17.3	11.4	35.8	20.6	13.7	8.4	5.1	58.3	32.8	22.2	15.1	11.4	45.8	25.1	18.0	13.7	10.6
700	97.5	56.5	41.0	27.6	19.3	12.9	37.8	22.4	15.2	9.8	5.6	62.7	36.1	24.4	16.7	12.7	49.8	27.3	19.4	15.0	11.8
800	98.1	62.8	44.1	30.4	21.6	15.0	41.7	24.5	17.8	12.3	6.8	68.3	40.4	27.5	19.4	14.4	55.1	31.3	20.7	15.4	13.1
900	98.4	68.9	49.5	34.1	24.3	17.7	46.5	26.9	20.4	14.9	9.4	73.4	44.8	31.1	22.2	16.7	61.6	36.1	23.7	17.7	15.1
1000	98.5	74.4	53.5	38.0	27.0	20.4	51.9	29.6	22.4	17.4	12.0	78.2	49.2	34.7	24.9	19.0	67.1	40.7	26.8	19.7	16.9
1100	98.5	78.4	57.6	41.1	29.3	22.2	56.6	32.3	24.0	19.0	14.5	81.3	52.7	38.0	27.3	20.8	71.4	45.1	29.8	21.6	18.5
1200	98.5	81.3	61.9	44.7	31.4	23.9	61.4	35.1	25.6	20.6	16.7	84.0	56.1	41.3	29.8	22.9	75.1	49.5	33.0	23.8	20.4
1500	98.5	87.6	73.0	55.5	38.4	28.4	73.0	44.9	30.7	24.4	21.6	89.4	65.5	49.9	37.6	28.5	83.8	61.9	43.3	30.9	28.1
2000	98.6	92.0	83.8	71.1	51.2	37.0	83.8	61.1	42.6	31.4	25.0	93.7	76.6	62.1	49.4	38.8	90.8	76.4	58.7	45.1	36.1
2500	98.6	93.8	89.2	80.9	63.0	46.7	88.6	72.4	54.4	40.1	28.1	95.7	83.8	71.2	58.7	47.9	94.2	84.4	70.2	57.5	47.7

IC80 dantes WALON 680 (POWDERED TEFLON)

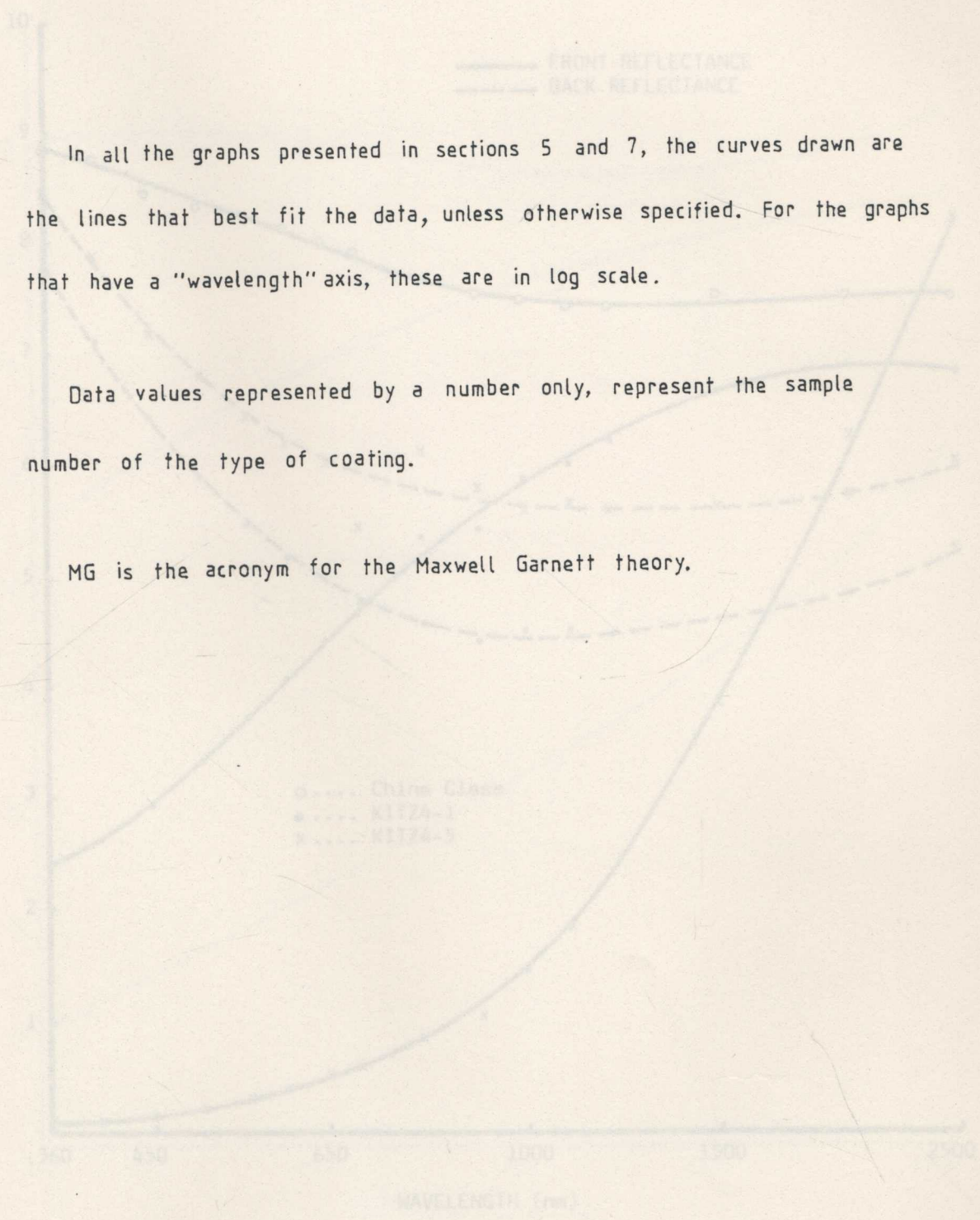
DIFFUSE REFLECTANCE (%) ON COPPER

WAVELENGTH (nm)	HG80	KITZ1					KITZ2					KITZ3					KITZ4				
		-1	-2	-3	-4	-5	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5
360	99.0	8.4	7.3	5.2	4.3	3.8	7.6	4.5	3.6	3.2	3.0	9.3	6.7	5.1	4.1	3.7	6.9	4.8	3.7	3.3	3.1
400	99.3	9.2	8.1	5.4	4.5	3.9	8.2	4.7	3.7	3.2	3.0	10.2	7.3	5.5	4.3	3.8	7.4	5.2	3.9	3.4	3.2
450	99.3	10.2	9.4	6.0	5.0	4.1	9.1	5.1	3.9	3.3	3.0	11.1	8.3	6.3	4.8	4.2	8.1	5.8	4.3	3.7	3.4
500	99.4	10.4	10.2	6.4	5.3	4.4	9.6	5.3	4.2	3.5	3.0	11.1	9.0	6.9	5.2	4.5	8.6	6.3	4.6	3.9	3.6
550	99.4	11.2	11.4	7.1	5.9	4.9	10.4	5.7	4.5	3.8	3.1	11.8	10.0	7.9	5.9	5.1	9.8	6.9	5.1	4.3	4.0
600	99.4	13.7	15.7	9.7	7.6	6.0	13.5	7.2	5.5	4.5	3.5	14.1	13.7	11.0	8.0	6.7	11.8	9.3	6.7	5.4	4.9
650	99.4	13.0	16.3	11.0	8.3	6.4	14.0	7.6	5.8	4.8	3.7	13.9	15.1	12.4	9.0	7.5	12.7	10.5	7.8	6.0	5.4
700	99.4	12.0	17.9	12.0	8.8	6.8	14.0	7.9	6.0	5.0	4.0	13.0	16.0	13.6	9.9	8.2	13.0	11.4	8.5	6.4	5.7
800	99.4	7.8	16.1	13.0	8.4	6.1	11.1	7.7	5.4	4.3	3.6	8.7	16.1	14.1	10.4	8.6	10.0	10.9	8.2	5.1	4.0
900	99.4	5.5	14.8	14.3	9.4	6.5	10.0	8.7	5.4	4.6	4.1	6.4	16.8	15.4	11.9	9.9	8.7	11.7	9.5	6.0	4.1
1000	99.4	3.9	13.0	15.1	10.7	7.1	9.2	9.7	6.0	4.8	4.4	4.8	16.9	16.9	13.2	11.1	7.5	12.0	10.8	7.0	4.8
1100	99.4	2.7	11.1	15.0	12.0	7.6	8.0	10.4	6.7	5.0	4.4	3.6	16.3	17.8	14.4	12.3	6.3	12.0	11.8	8.0	5.4
1200	99.3	1.8	9.5	14.7	13.4	8.4	6.9	11.1	7.7	5.2	4.3	2.6	15.7	18.7	15.8	13.8	5.1	11.4	13.0	9.0	6.1
1500	99.2	0.5	4.8	11.2	16.1	11.4	4.1	11.1	10.6	6.6	5.8	1.0	11.9	19.3	19.3	17.3	2.5	8.9	14.8	12.3	9.4
2000	98.1	0.2	1.2	5.0	14.7	16.7	1.5	8.1	12.7	11.6	8.8	0.4	6.0	16.1	22.1	22.9	1.1	4.0	13.1	14.0	13.6
2500	96.0	0.1	0.5	1.7	10.3	17.3	0.6	4.7	10.7	14.6	10.2	0.2	2.6	11.7	20.8	26.6	0.9	1.3	9.4	11.8	13.3

HG80 dentes HALON G80 (POWDERED TEFLON)

GRAPH 5.1

FILM SPECULAR REFLECTANCE (ON GLASS) VERSUS WAVELENGTH



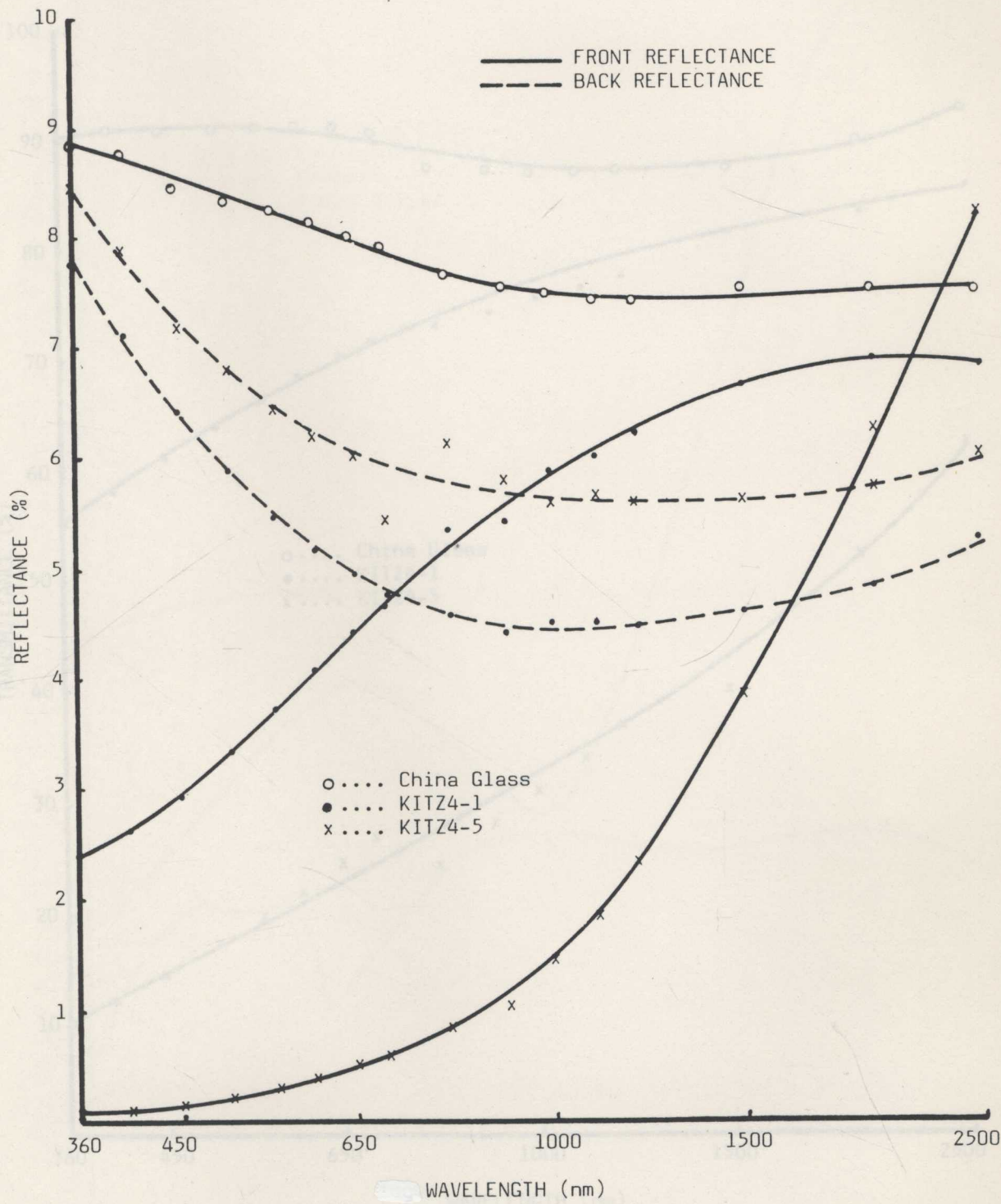
In all the graphs presented in sections 5 and 7, the curves drawn are the lines that best fit the data, unless otherwise specified. For the graphs that have a "wavelength" axis, these are in log scale.

Data values represented by a number only, represent the sample number of the type of coating.

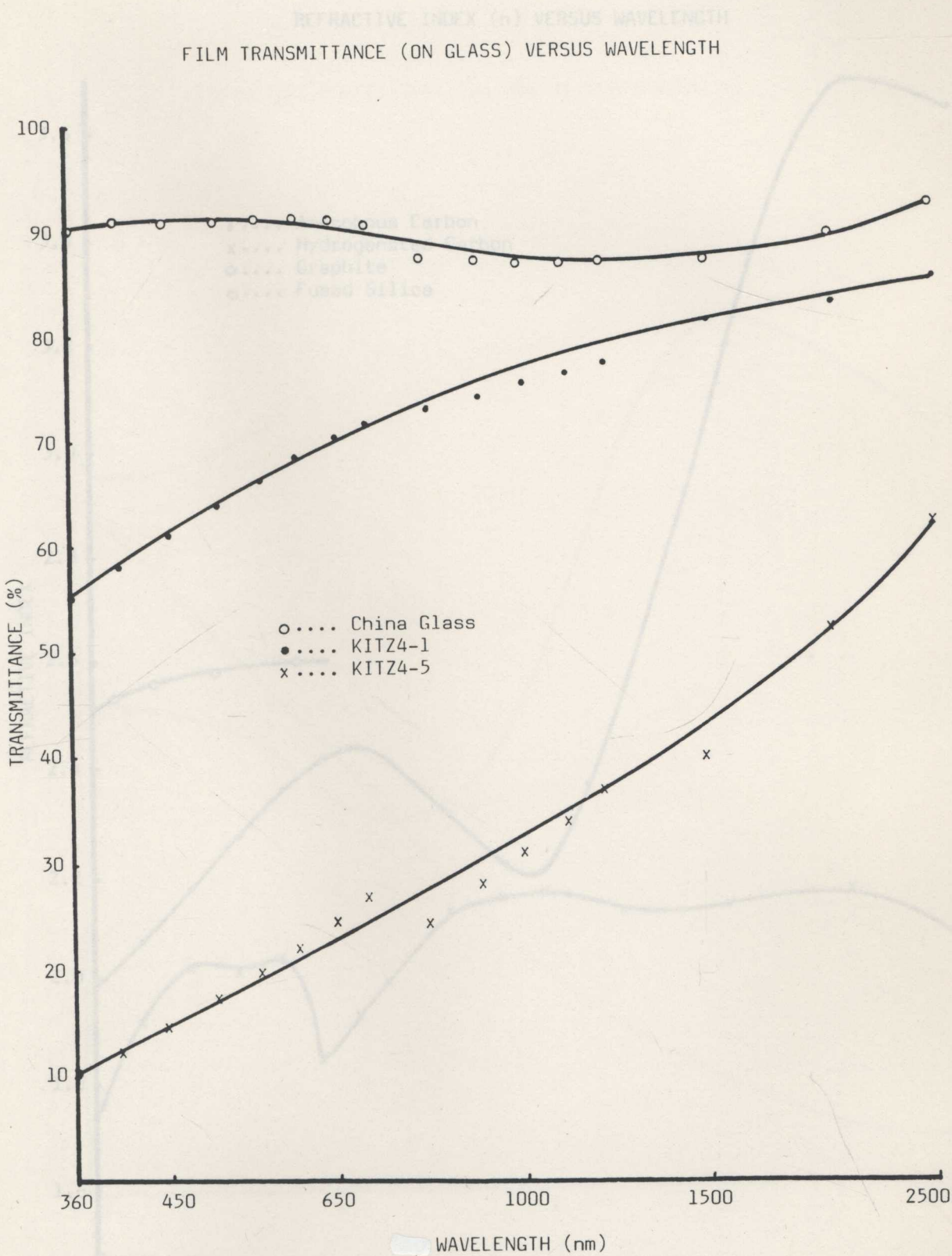
MG is the acronym for the Maxwell Garnett theory.

GRAPH 5.1

FILM SPECULAR REFLECTANCE (ON GLASS) VERSUS WAVELENGTH

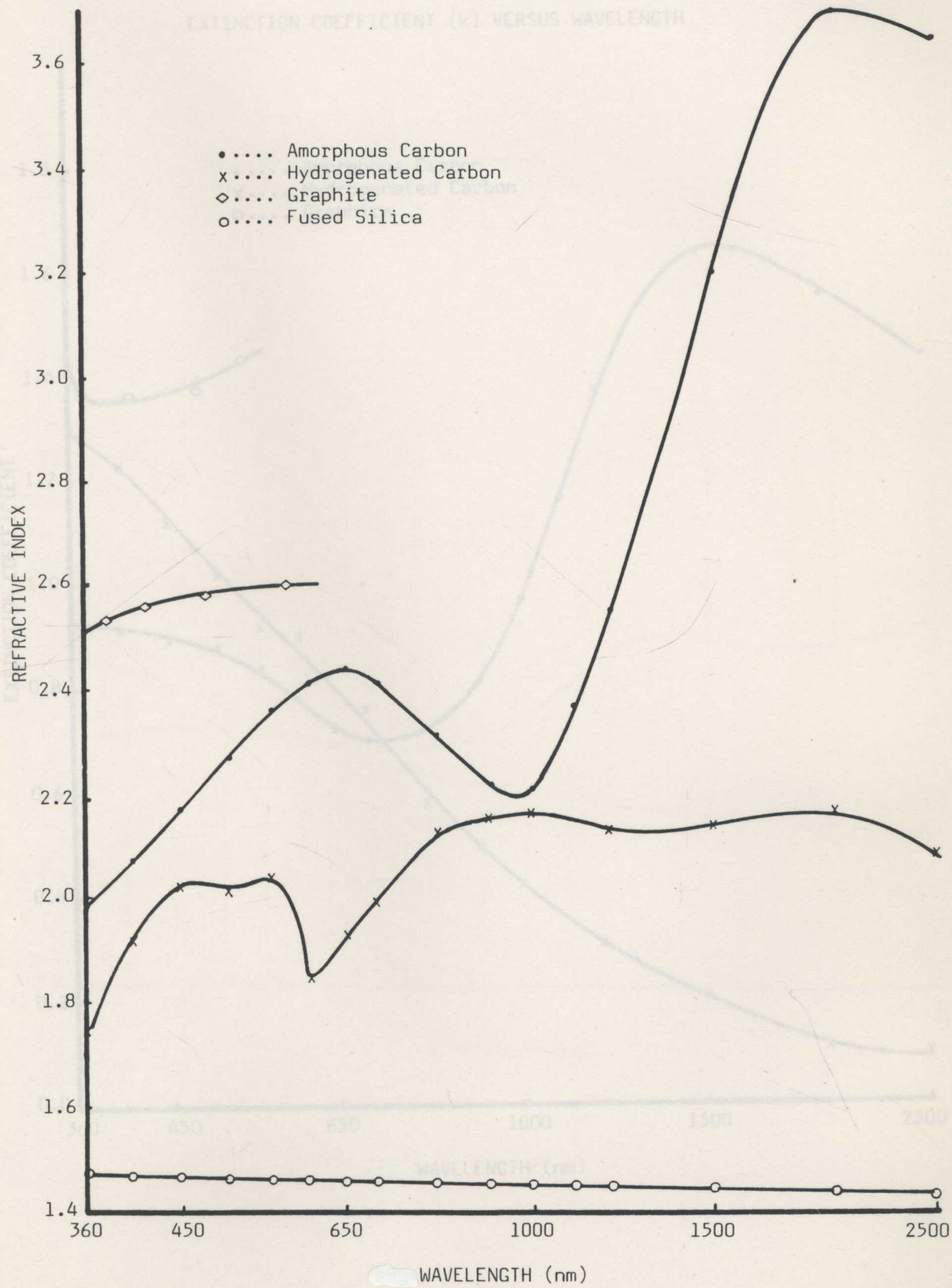


GRAPH 5.2



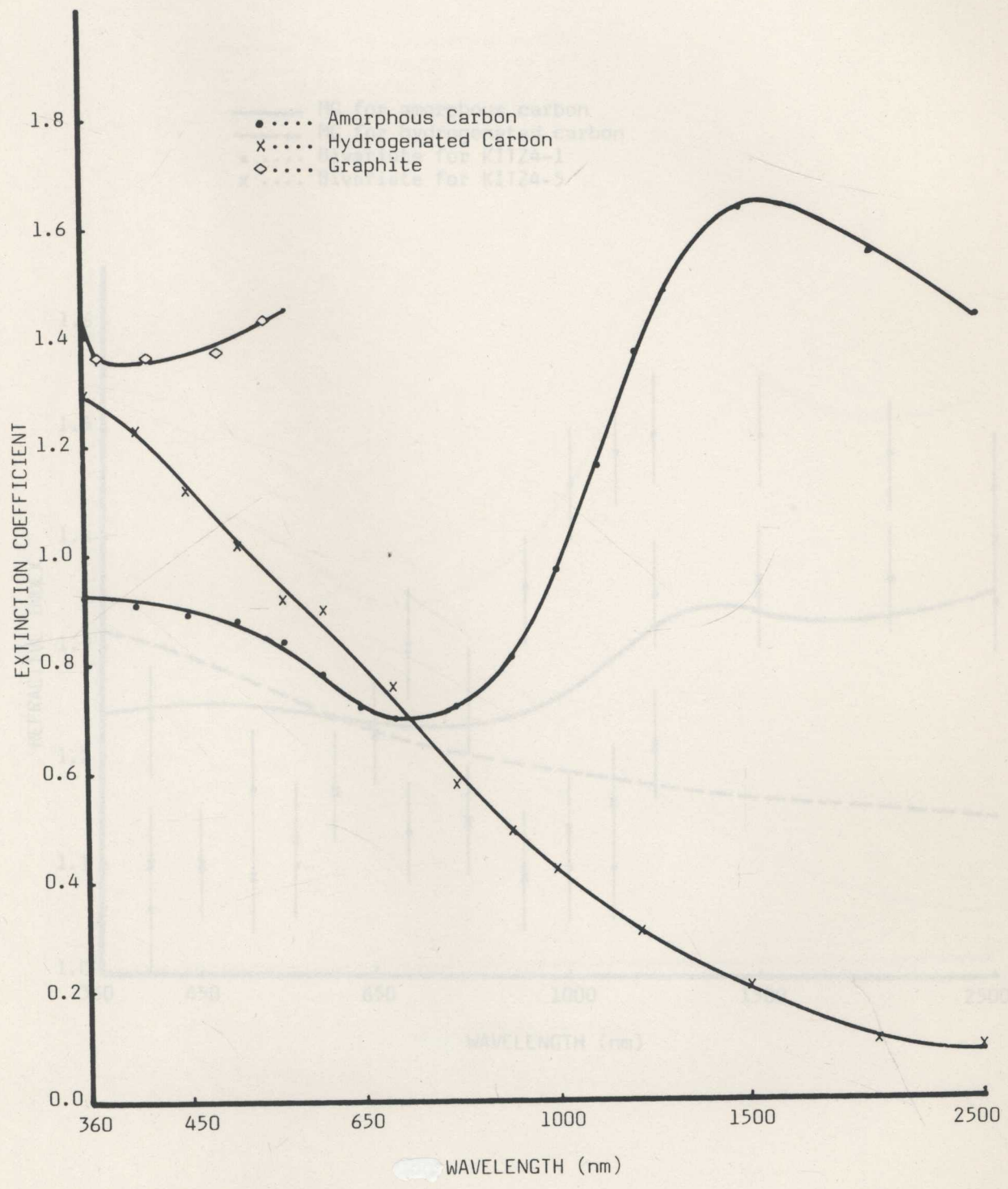
GRAPH 5.3

REFRACTIVE INDEX (n) VERSUS WAVELENGTH



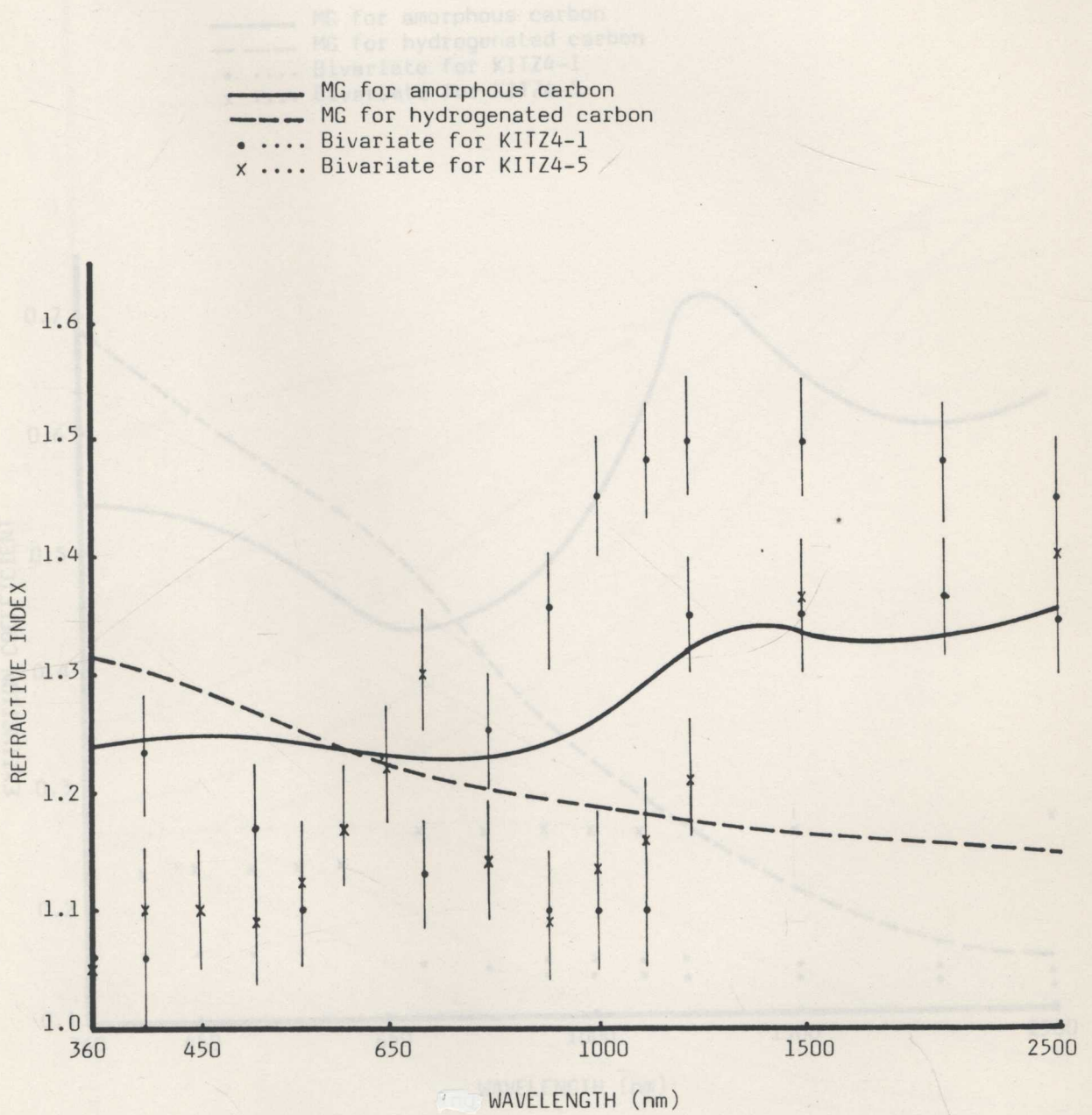
GRAPH 5.4

EXTINCTION COEFFICIENT (k) VERSUS WAVELENGTH



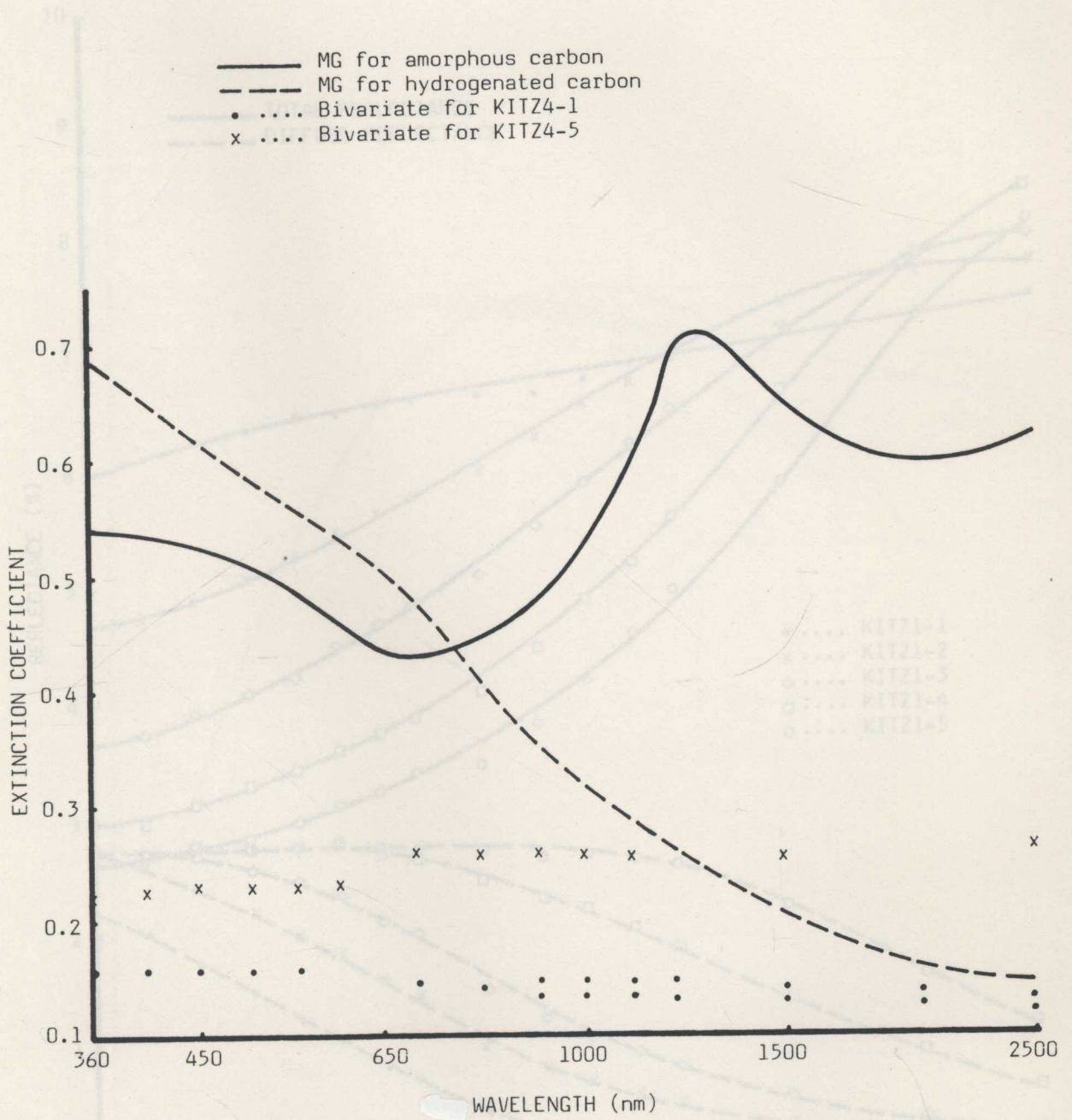
GRAPH 5.5

REFRACTIVE INDEX (n) OF MEDIUM
VERSUS WAVELENGTH



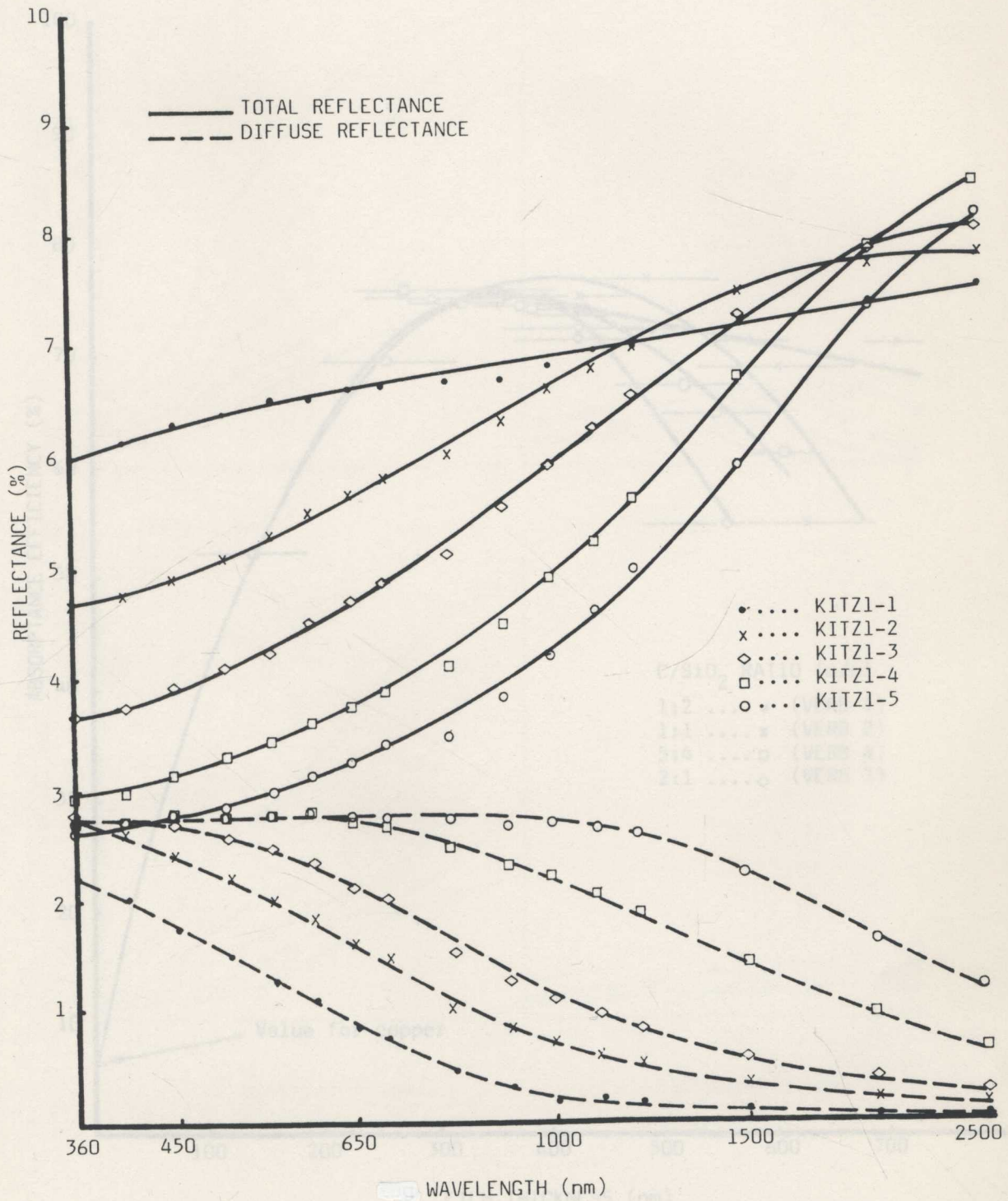
GRAPH 5.6

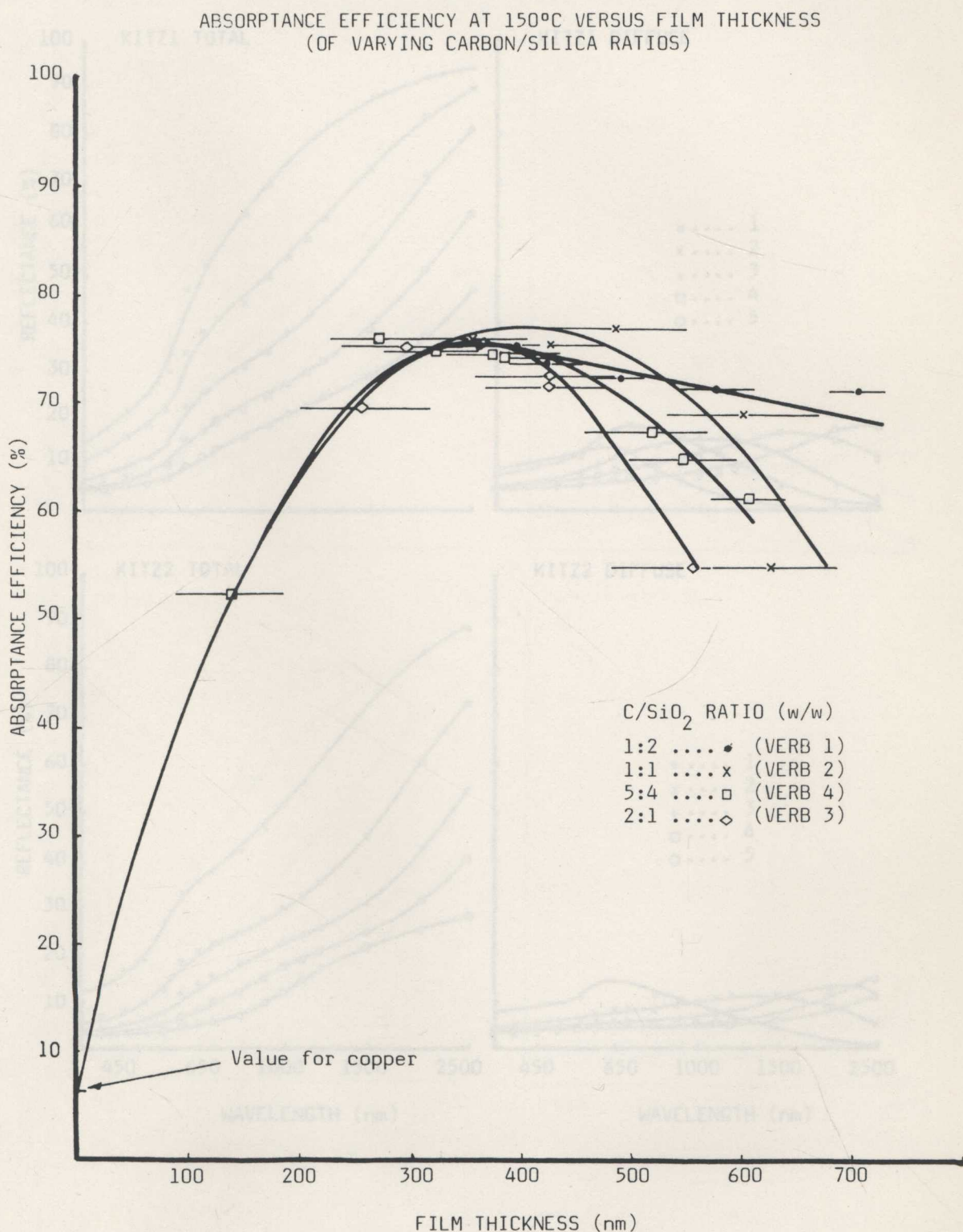
EXTINCTION COEFFICIENT (k) OF MEDIUM (ON GLASS)
VERSUS WAVELENGTH



GRAPH 5.7

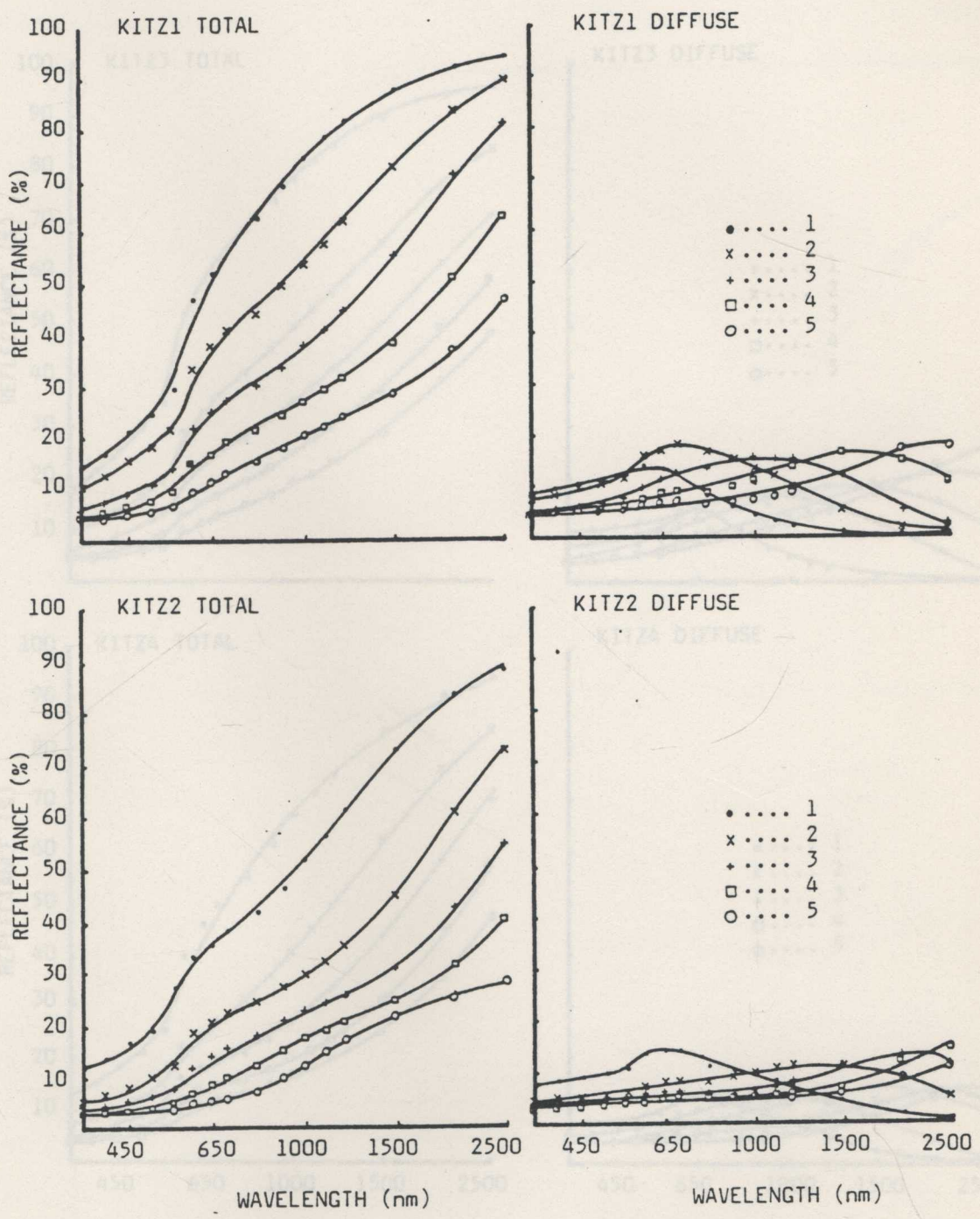
COMPARISON OF TOTAL AND DIFFUSE REFLECTANCE (ON GLASS)
VERSUS WAVELENGTH





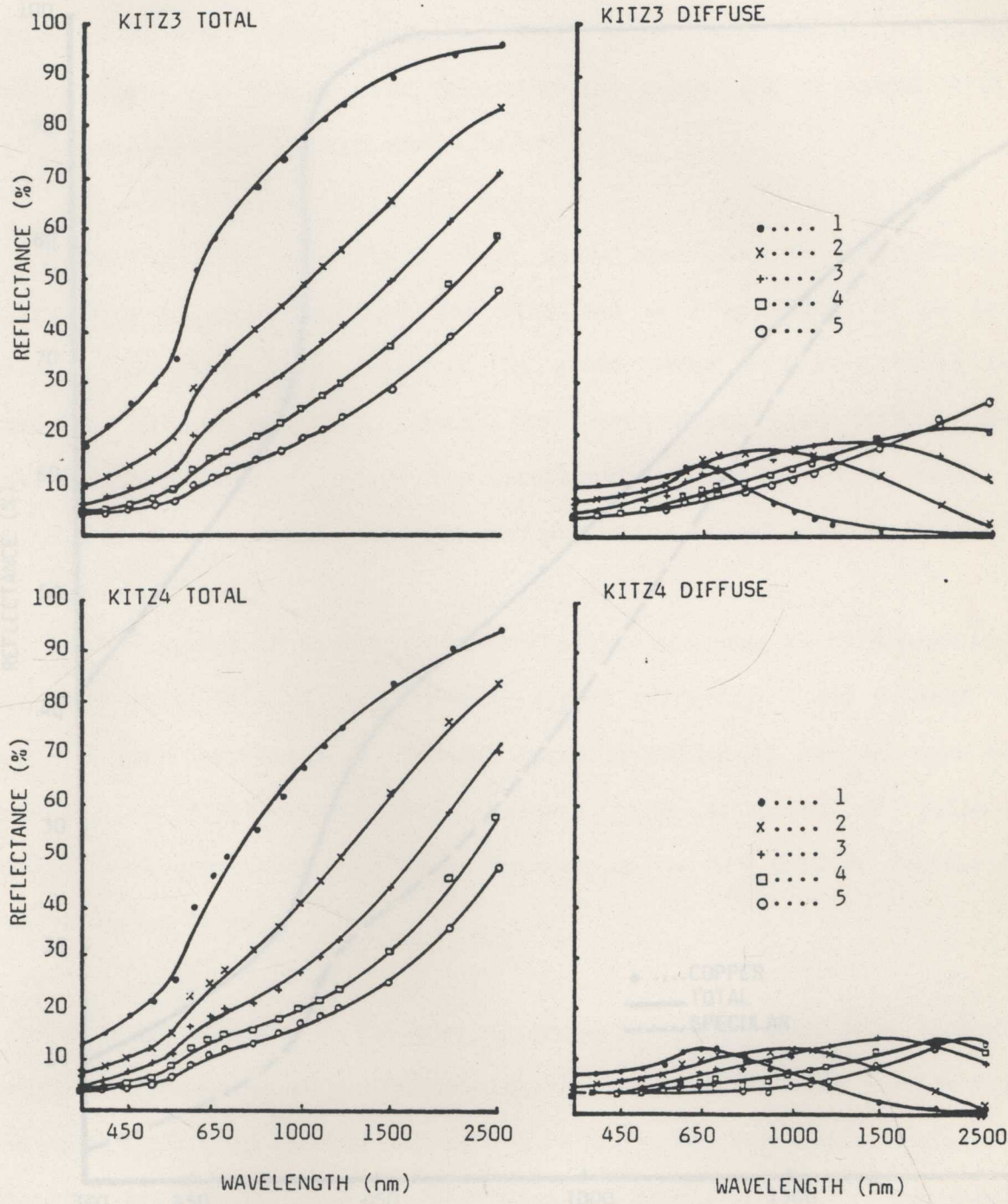
GRAPH 5.9a

REFLECTANCE OF COATINGS ON COPPER VERSUS WAVELENGTH



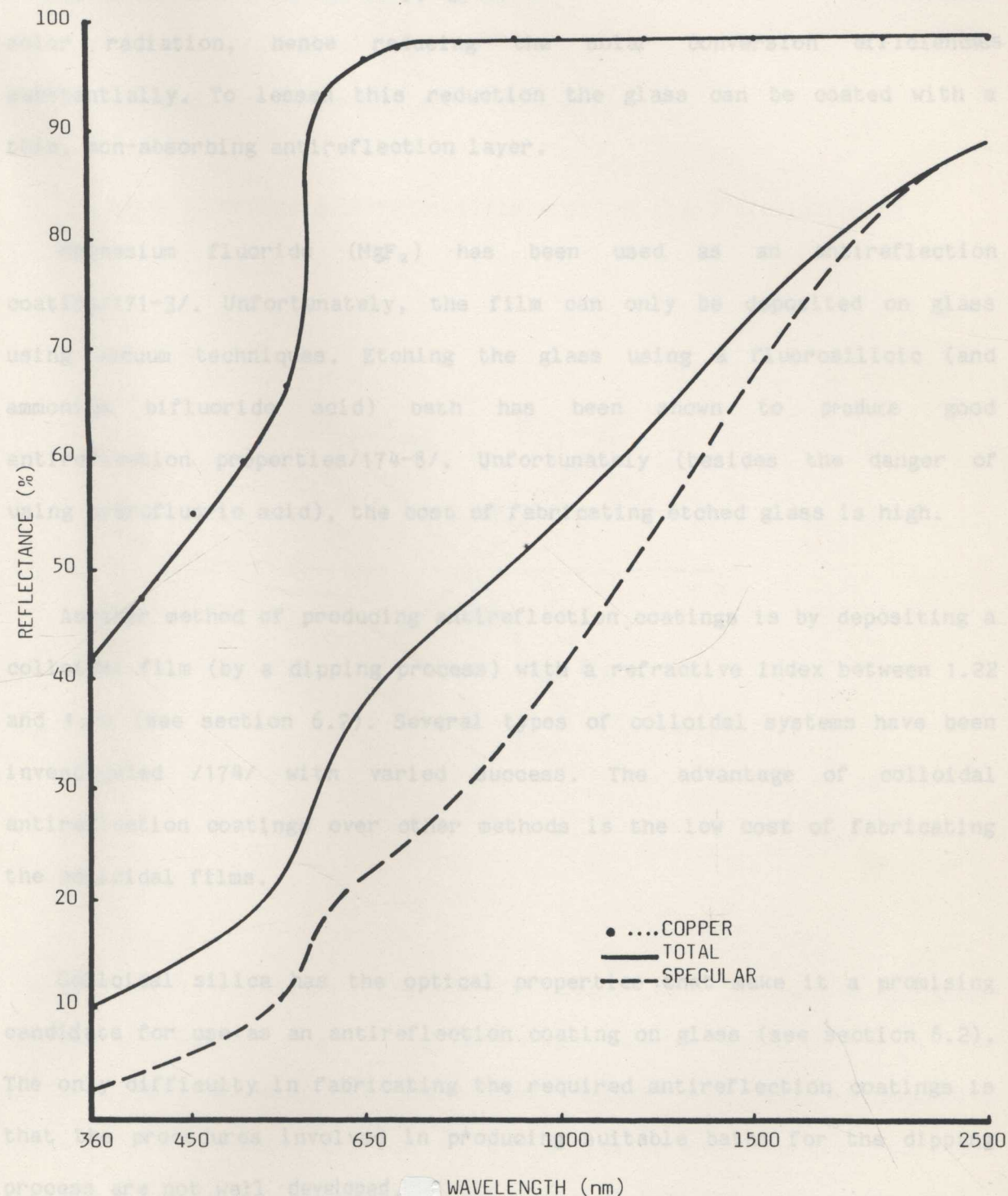
GRAPH 5.9b

REFLECTANCE OF COATINGS ON COPPER VERSUS WAVELENGTH



GRAPH 5.10

COMPARISON OF TOTAL AND SPECULAR REFLECTANCE OF KITZ1-2 (ON Cu)
VERSUS WAVELENGTH



SECTION 6

ANTIREFLECTION COATINGS

Glass covers are commonly used to protect photothermal surfaces from the environment. Unfortunately, glass reflects about 8% of the incident solar radiation, hence reducing the solar conversion efficiencies substantially. To lessen this reduction the glass can be coated with a thin, non-absorbing antireflection layer.

Magnesium fluoride (MgF_2) has been used as an antireflection coating [171-3]. Unfortunately, the film can only be deposited on glass using vacuum techniques. Etching the glass using a fluorosilicic (and ammonium bifluoride acid) bath has been shown to produce good antireflection properties [174-8]. Unfortunately (besides the danger of using hydrofluoric acid), the cost of fabricating etched glass is high.

Another method of producing antireflection coatings is by depositing a colloidal film (by a dipping process) with a refractive index between 1.22 and 1.26 (see section 6.2). Several types of colloidal systems have been investigated [174] with varied success. The advantage of colloidal antireflection coatings over other methods is the low cost of fabricating the colloidal films.

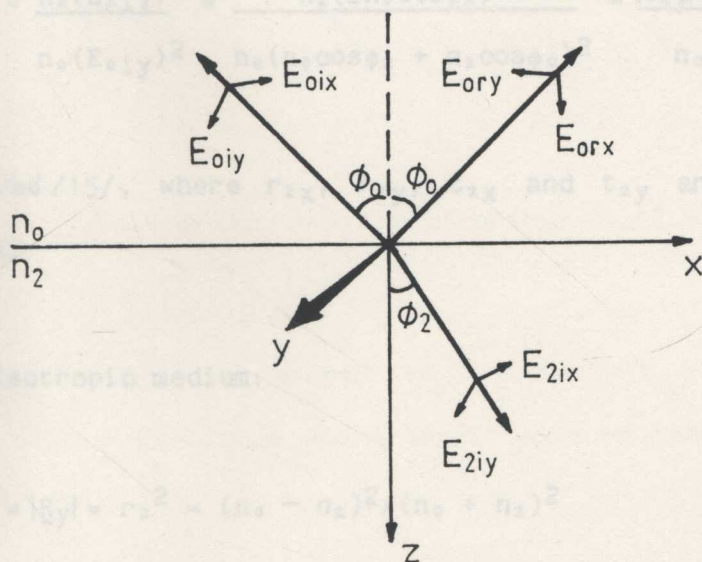
Colloidal silica has the optical properties that make it a promising candidate for use as an antireflection coating on glass (see section 6.2). The only difficulty in fabricating the required antireflection coatings is that the procedures involved in producing suitable baths for the dipping process are not well developed.

6.1 THEORY OF ANTIREFLECTION COATINGS

Before determining the reflectance and transmittance of light by a non-absorbing film on glass, the reflectance and transmittance at the glass/air interface has to be known first.

6.1.1 THE GLASS/AIR INTERFACE (see figure 6.1)

FIGURE 6.1 REFLECTANCE/TRANSMITTANCE AT THE GLASS/AIR INTERFACE



Consider the electric field vector of light ($\underline{E}_o$) incident at the glass surface defined by a x, y, z, co-ordinate system where $z = 0$ at the surface. The reflected and transmitted light will have corresponding electric field vectors $\underline{E}_r$ and $\underline{E}_t$ respectively. When the electric field vectors are expressed in terms of the the x, y amplitude components (E_{oix} , E_{oiy} , E_{oirx} , E_{oiry} , E_{tix} , E_{tiy}) the following expressions for the reflectances:

$$|R_x| = \frac{(E_{0rx})^2}{(E_{0ix})^2} = \frac{(n_0 \cos \phi_2 - n_1 \cos \phi_0)^2}{(n_0 \cos \phi_2 + n_1 \cos \phi_0)^2} = (r_{2x})^2 \quad (6.1)$$

$$|R_y| = \frac{(E_{0ry})^2}{(E_{0iy})^2} = \frac{(n_0 \cos \phi_0 - n_2 \cos \phi_2)^2}{(n_0 \cos \phi_0 + n_2 \cos \phi_2)^2} = (r_{2y})^2 \quad (6.2)$$

and the transmittances:

$$|T_x| = \frac{n_2 (E_{2ix})^2}{n_0 (E_{0ix})^2} = \frac{n_2 (2n_0 \cos \phi_2)^2}{n_0 (n_0 \cos \phi_0 + n_2 \cos \phi_2)^2} = \frac{(t_{2x})^2 n_2}{n_0} \quad (6.3)$$

$$|T_y| = \frac{n_2 (E_{2iy})^2}{n_0 (E_{0iy})^2} = \frac{n_2 (2n_0 \cos \phi_2)^2}{n_0 (n_0 \cos \phi_2 + n_2 \cos \phi_0)^2} = \frac{(t_{2y})^2 n_2}{n_0} \quad (6.4)$$

can be established /15/, where r_{2x} , r_{2y} , t_{2x} and t_{2y} are known as Fresnel coefficients.

For an isotropic medium:

$$|R_x| = |R_y| = r_2^2 = (n_0 - n_2)^2 / (n_0 + n_2)^2 \quad (6.5)$$

and

$$|T_x| = |T_y| = t_2^2 = 4n_0 n_2 / (n_0 + n_2)^2 \quad (6.6)$$

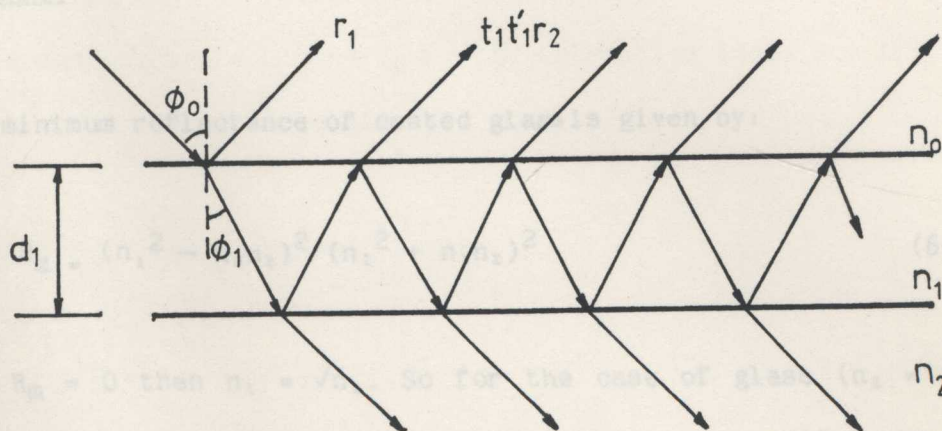
where r_2 and t_2 are the Fresnel coefficients for the reflectance and transmittance, respectively, of glass (with a refractive index n_2).

6.1.2 THIN NON-ABSORBING FILM ON GLASS

To attempt to determine the reflectance and transmittance of coated glass, one must consider the multiple reflections (and resulting

transmissions) of the layer (see figure 6.2).

FIGURE 6.2 REFLECTANCES/TRANSMITTANCES OF A NON-ABSORBING COATING ON GLASS



(from the conservation of energy $t_1 t_1' = 1 - r_1^2$)

By assuming that the product of the Fresnel coefficients are very small, the total reflectance and transmittance of the coated glass can be shown /15/ to be:

$$|R| = (r_1^2 + 2r_1 r_2 \cos 2\delta_1 + r_2^2) \quad (6.7)$$

and

$$|T| = n_2(1 + r_1 + r_2)^2/n_0 \quad (6.8)$$

where

$$r_1 = (n_0 - n_1)/(n_0 + n_1) \quad (6.8a)$$

and

$$r_2 = (n_1 - n_2)/(n_1 + n_2) \quad (6.8b)$$

and δ_1 is the phase change experienced by light in the non-absorbing layer

and is given by: Yoldas /179/ the relation between the density and

refractive index of a porous and non-porous medium is given by:

$$\delta_1 = (2\pi n_1 d_1 \cos \phi_1) / \lambda \quad (6.9)$$

$$(n_p^2 - 1) / (n^2 - 1) = \rho_p / \rho \quad (6.11)$$

6.2 THE REFRACTIVE INDEX REQUIRED TO OBTAIN AN ANTIREFLECTION COATING

ON GLASS

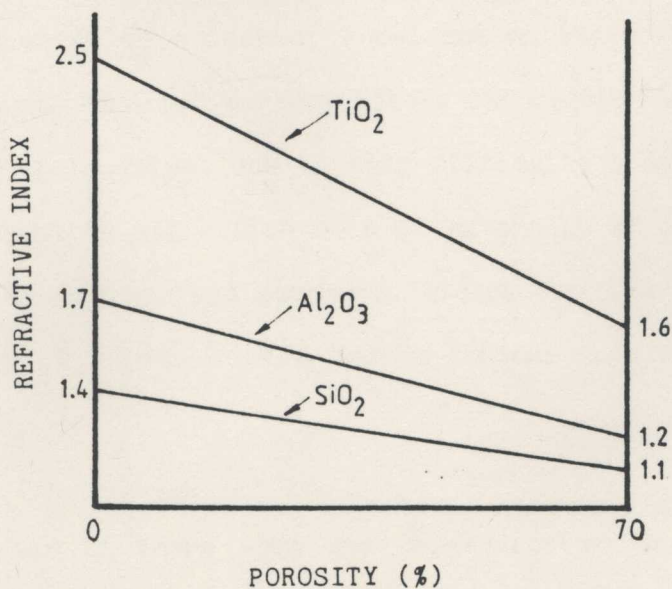
are the refractive index and the density, respectively, of the non-porous medium, while ρ_p and ρ are the refractive index and the density,

The minimum reflectance of coated glass is given by:

$$R_m = (n_1^2 - n_0 n_2)^2 / (n_1^2 + n_1 n_2)^2 \quad (6.10)$$

For $R_m = 0$ then $n_1 = \sqrt{n_2}$. So for the case of glass ($n_2 = 1.52$) the refractive index of the antireflection must be approximately 1.23. No single inorganic material has such a low refractive index. Magnesium fluoride is the closest with a value of 1.38. A method to achieve a lower refractive index is to decrease the density of an inorganic film, that is, promote pores or voids (see figure 6.3). Alternatively, the use of colloids can solve the problem.

FIGURE 6.3 EFFECT OF POROSITY ON REFRACTIVE INDEX /179/



According to Yoldas /179/ the relation between the density and refractive index of a porous and non-porous medium is given by:

$$(n_p^2 - 1)/(n^2 - 1) = d_p/d \quad (6.11)$$

where n and d are the refractive index and the density, respectively, of the non-porous medium, while n_p and d_p are the refractive index and the density, respectively, of the porous medium.

Equation 6.11 can be re-written as:

$$P = 1 - (n_p^2 - 1)/(n^2 - 1) \quad (6.12)$$

where P is the porosity fraction.

7.1 EXPERIMENTAL CHARACTERISATIONS OF THE COATINGS.

7.1.1 PREPARATION OF THE COLLOIDAL SOL.

For the case of coating glass with colloidal silica ($n = 1.46$) the porosity of the coating must optimally be 0.54.

The dilution and flocculation of commercially available aquasols was required so as to produce a bath capable of fabricating an antireflection coating (see section 5). The recipe used was similar to the one described by Cathers, Constable and Solaga /174/, although their exact procedure could not be repeated owing to a lack of knowledge of the precise definition of their term "optical density" as very little information was given about the determination of this value. Due to this difficulty a systematic procedure was used that required all silica sols to have a pH of 2 immediately after the dilution with ethanol and methanol, except for the sample LACH4 which was aged at a pH of 7 for 16 hours before further acidification to a pH of 2.

To investigate if there were any dependence on the primary particle size of the colloidal silica with the antireflection properties, various

SECTION 7

CHARACTERISATION OF COLLOIDAL SILICA ANTI-REFLECTION COATINGS.

The purpose of this investigation was to characterise the colloidal silica antireflection coatings and determine the conditions which produce the optimum coating. It was hoped that the optical and physical studies of the colloidal silica films of varying silica primary particle size and varying film thickness would result in a technique for fabricating this optimum coating.

Previous work /174/ has been done on the effect of high temperatures on these coatings. Consequently no studies of this nature were done in this project.

7.1 EXPERIMENTAL CHARACTERISATIONS OF THE COATINGS.

7.1.1 PREPARATION OF THE COLLOIDAL SOL.

The dilution and flocculation of commercially available aquasols was required so as to produce a bath capable of fabricating an antireflection coating (see section 6). The recipe used was similar to the one described by Cathro, Constable and Solaga /174/, although their exact procedure could not be repeated owing to a lack of knowledge of the precise definition of their term "optical density" as very little information was given about the determination of this value. Due to this difficulty a systematic procedure was used that required all silica sols to have a pH of 2 immediately after the dilution with ethanol and methanol, except for the sample LECH4 which was aged at a pH of 7 for 16 hours before further acidification to a pH of 2.

To investigate if there were any dependence on the primary particle size of the colloidal silica with the antireflection properties, various

silica aquasols were studied. They were obtained from:

(I) Monsanto Chemicals Inc..... Syton X-30

(ii) Catoleum Chemicals Pty Ltd..... PR4850, 1030 and 7604.

The primary particle sizes were calculated from electron microscopy studies (see figures 7.1 to 7.4) and the following values were obtained.

SAMPLE	AVERAGE PARTICLE DIAMETER (nm)
LECH 1 (PR4850)	5 ± 2
LECH 2 (1030)	16 ± 3
LECH 3 (SYTON X-30)	22 ± 6
LECH 4 (SYTON X-30)	22 ± 6
LECH 5 (7604)	75 ± 9

The colloidal silica antireflection coatings were fabricated by immersing and withdrawing (with constant velocity) clean Corning 2947 microscope glass slides (see section 7.1.2) into and out of the alkanol diluted colloidal silica sols (known hereafter as "silica bath") using the withdrawal apparatus illustrated in figure 5.1. Variation of the withdrawal velocity enabled the different film thicknesses to be produced (see table 7.1).

7.1.2 SLIDE PREPARATION AND MEASUREMENT

The cleaning of the "Crown Corning 2947" microscope glass slides involved the same procedures as discussed in section 5.2.1. Reflectance, transmittance, film thickness and density calculations were also identical to the procedures described in section 5.2 except that the transmittance measurements were done on a Varian Cary 2300 spectrophotometer and no

diffuse reflectances were observed of the coatings.

7.2 OPTICAL CHARACTERISATIONS OF COLLOIDAL SILICA ANTIREFLECTION COATINGS

7.2.1 REFRACTIVE INDEX

The reflectances of the antireflection coatings on glass (see table 7.2 and graphs 7.1) were used to evaluate the refractive indices (see section 6). The reflectances were chosen in preference to the transmittances because the former were more sensitive to the degree of annulment of reflection and hence a better indication of the trends was obtained. The errors quoted are representative of the scatter of the results and not of the "absolute" errors.

Equation 6.10 was derived for a non-absorbing medium, and is applicable in this case as the absorptances of the films observed were very small, typically $(0.4 \pm 0.3)\%$ of the solar radiation (for two coatings) over the whole wavelength region (see tables 7.2 to 7.4 for the comparisons, noting that Corning 2947 glass was observed to absorb $(0.6 \pm 0.3)\%$ of the solar radiation, see table 7.3). Consequently this should not invalidate the assumptions made in calculating the refractive indices of the coatings.

7.2.2 SOLAR TRANSMITTANCE

The solar transmittances of the colloidal coatings (on Corning 2947 glass slides) were calculated, as this is the quantity of direct interest in solar thermal conversion. The coatings fabricated from each colloidal silica bath (see table 7.5) which had the lowest reflectance minima around 600 nm to 700 nm were used to calculate the solar transmittance. This involved the summation of transmitted intensities of 16 wavelengths between 360 nm to 2500 nm. This selection criterion was not used

except for LECH4-3 which was the best antireflection coating from the LECH4 batch even though the minimum ^{was} near 800 nm. The wavelength range of 600 nm to 700 nm was chosen because the peak of the incident solar flux /180/ lies in that range (see graph 7.7).

7.3 DISCUSSION OF RESULTS

7.3.1 DEPENDENCE ON PARTICLE SIZE

An interesting behaviour of the colloidal silica antireflection coatings was observed. There appeared to be a dependence of the minimum reflectance and, consequently, the refractive index (at 650 nm) on silica primary particle size (see table 7.6 and graphs 7.4, 7.5). The minimum reflectances were determined from the curves that had a minimum near 650 nm or the value at 650 nm if the minima were not near 650 nm (e.g. LECH4-3)(see graphs 7.1). The refractive indices, as a function of silica primary particle size, were calculated from the determined minimum reflectances at 650 nm by using equation 6.10. Although two refractive indices can be calculated for each reflectance, the choice of the correct refractive index was made on the basis of the behaviour of density with particle size i.e. a decrease in the film density (see graph 7.2) led to a decrease in the refractive index. Consequently, the graphical plot of the refractive index (at 650 nm) versus silica particle size (see graph 7.5) exhibited a continuous curve where the optimum refractive index ($n = 1.23$, see section 6.2) occurred for a coating containing colloidal silica, 45 nm in diameter.

A plot of the solar transmittance through coated Corning 2947 glass also showed this behaviour (see graph 7.6). Unfortunately, the results obtained are not necessarily of the best possible antireflection coatings fabricated from each silica bath, but it would be safe to assume that all

but LECH4 (and LECH3) were very close to the best coatings because the shapes and positions of the spectral profiles were similar to that of the incident solar spectrum (air mass = 1). Consequently, the choice of the "curve of best fit" involved LECH1, LECH2, LECH5 and the reported result of Cathro, et al /174/, with LECH4 (and LECH3) omitted. It was interesting to observe that the Corning 2947 glass itself seemed to exhibit slight antireflection properties. It is unlikely that a layer of Decon-90 caused this behaviour because when Schott B270 glass, cleaned with Decon-90, was investigated it did not show this same behaviour. It is probable that the Corning 2947 glass surface is slightly porous.

To further verify that the fabricated coatings were close to the best antireflection coatings possible for each silica size, attempts were made to induce further flocculation of the silica colloids by slowing the acidification procedure, as was done by Cathro, et al /174/ and in this work on LECH3 and LECH4 (see section 7.1.1). The LECH3 silica bath was produced in the same manner as the three other silica baths and the LECH3 coating was observed to have antireflection properties poorer than those obtained from the LECH4 silica bath. Unfortunately, when this same procedure was attempted for LECH1 and LECH2, semi-opaque coatings were produced. Based on these observations it seems plausible to suggest that the coatings fabricated from the LECH1, LECH2, LECH4 and LECH5 silica baths are close to the optimum porosities possible for these colloidal silica films.

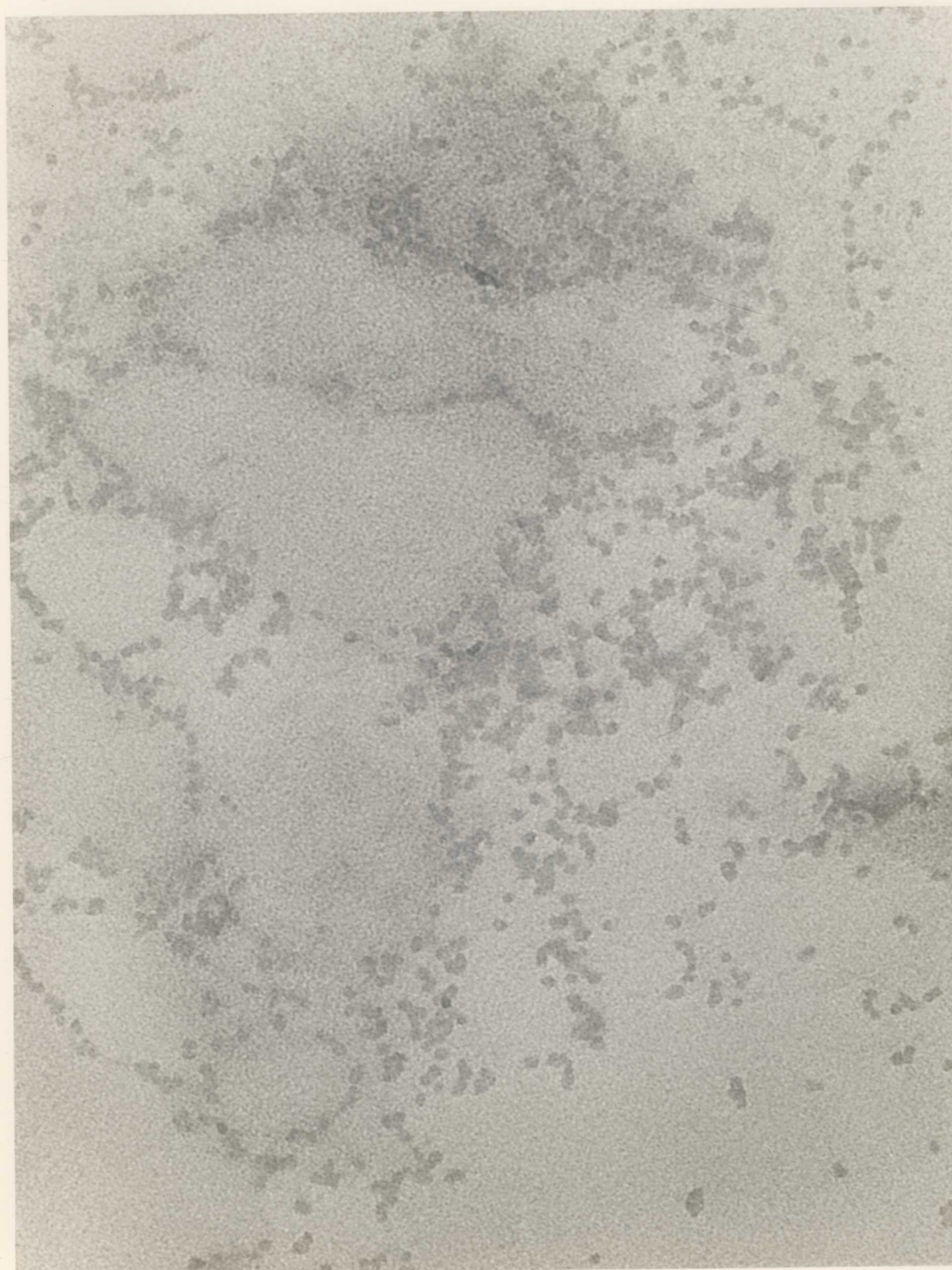
Possible reasons for the optimum transmittance (and minimum reflectance) dependence on silica primary particle size and the high extrapolated density value (see graph 7.3) of the optimum antireflection coating (high in comparison to the value using equation 6.11) are attributable to interstitial water or solute entrapment in the coatings from either atmospheric water vapour or solvent or solute retention from

the coating baths. The colloidal silica aquasols used in this project contain appreciable amounts of silica monomers because of the procedures required to produce these colloidal silica aquasols /183/. It is therefore possible that the monomer solute (and water solvent) is trapped between the colloidal particle so that the smaller colloids adsorb more of the monomer (per unit volume) than the larger colloids because of the larger surface area of the former. The electron microscopy pictures (see figures 7.1 to 7.4) support this suggestion by the visual evidence of trapped solvents that exist in the smaller silica particles that are not as prevalent in the larger silica colloids. The degree of monomer adsorption also explains the density dependence on silica particle size which, in turn, also explains the dependence of minimum reflectance on silica particle size.

Netterfield et al /181/ and Yoldas /179/ have observed that thin porous films absorb significant amounts of water from the atmosphere, where Yoldas has reported the increase of the reflectances of these films. The water absorption affects the optical properties of the coatings because the environment surrounding the colloidal silica is no longer just air (with $n = 1.00$) but a mixture of air and water of unknown concentration and this also explains the high density value extrapolated for the optimum coating.

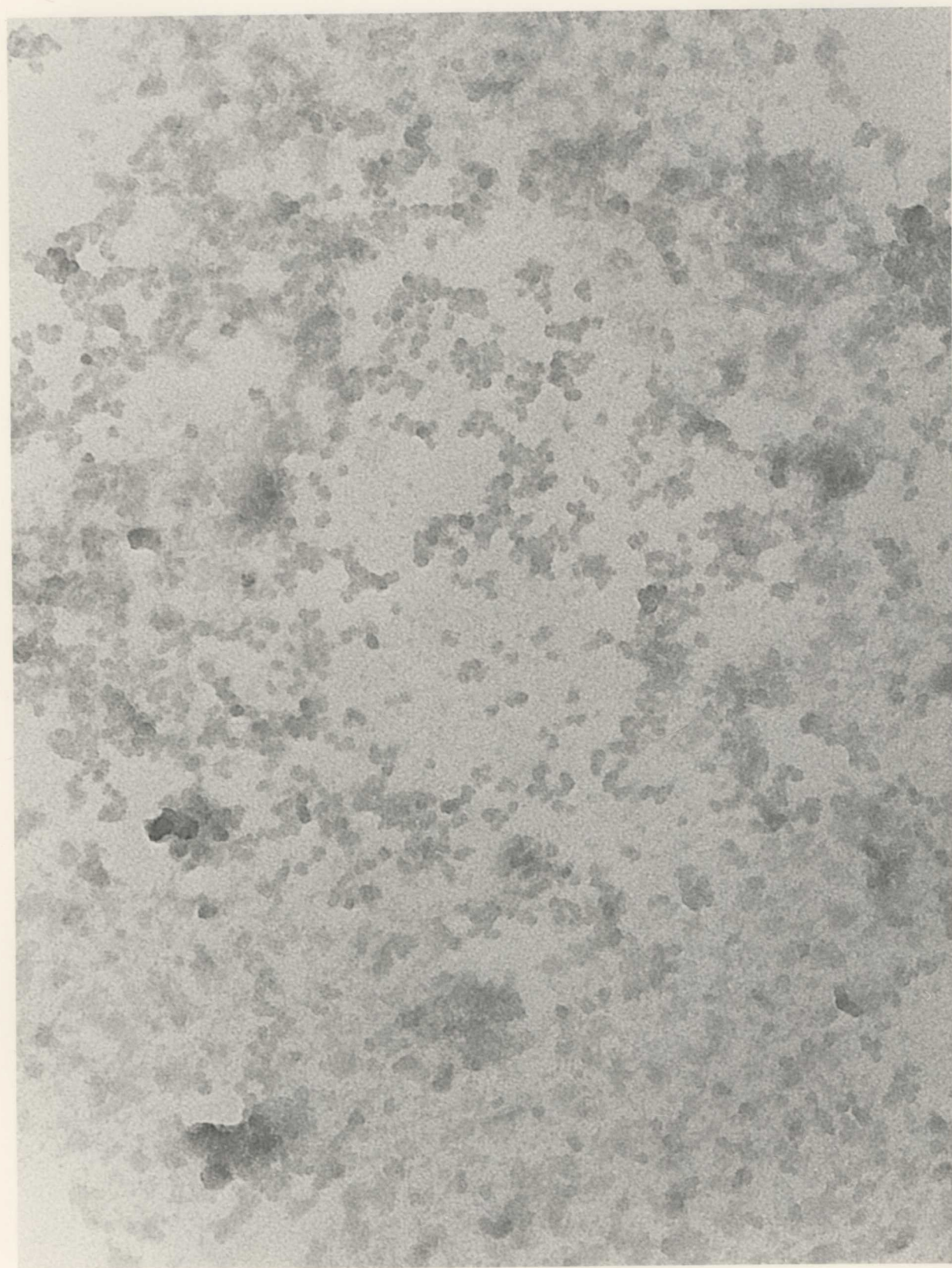
In conclusion, from the graphical plots 7.4 to 7.6 it can be predicted that the ideal colloidal silica antireflection coating can be fabricated from a bath containing water, acid, ethanol, methanol and colloidal silica with a primary particle size around 45 nm in diameter. This may produce a coated (Corning 2947) glass cover with approximately 99% solar transmittance. Alternatively, a mixture of small and large silica colloids (with refractive indices above and below the optimum refractive index respectively) in the film could fabricate a coating with the appropriate refractive index required to produce the optimum antireflection coating.

FIGURE 7.1a LECH1 /186/



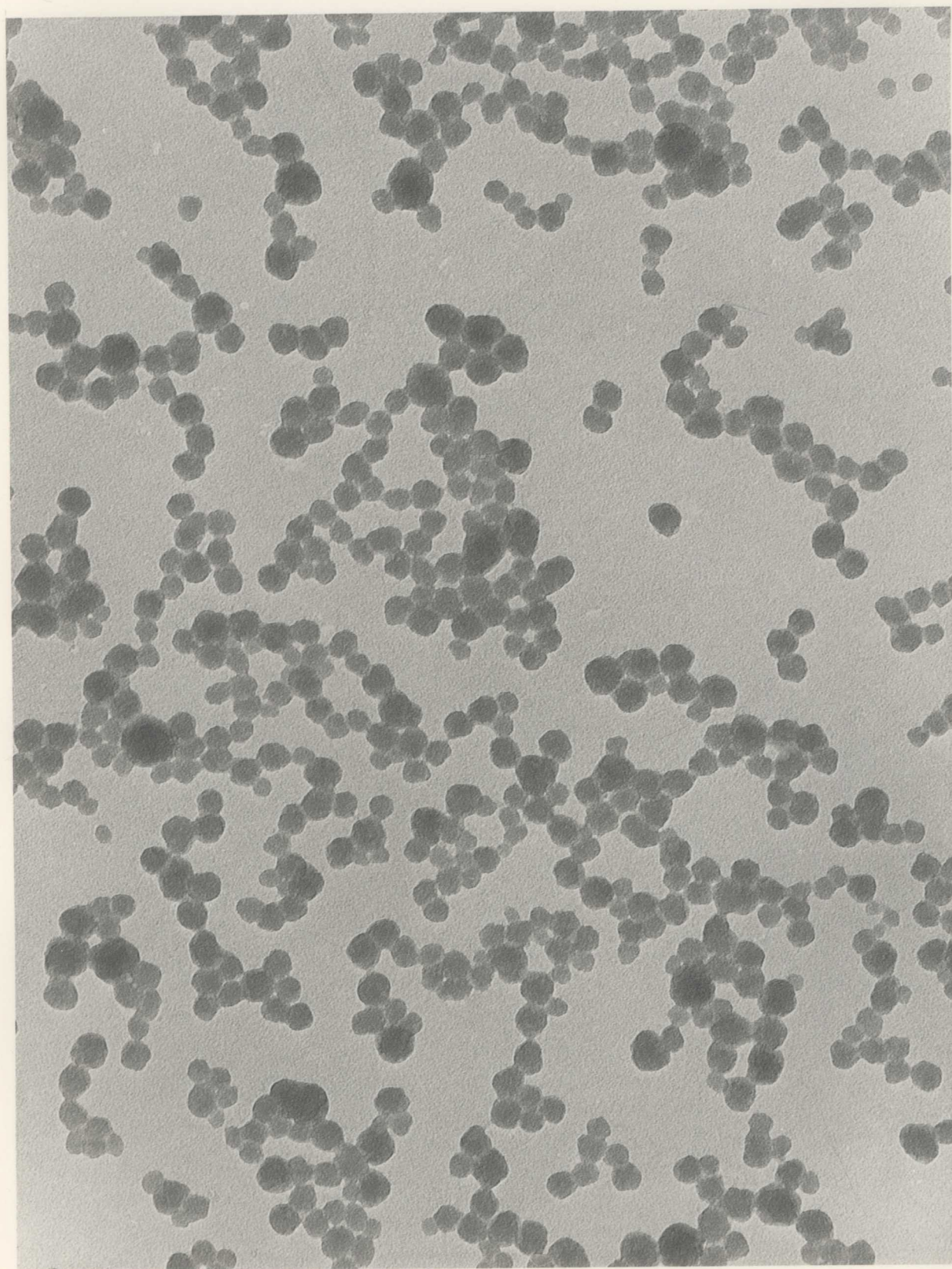
50 nm

FIGURE 7.1b LECH1 /186/



50 nm

FIGURE 7.2 LECH2 /186/ *et al.*



50 nm

FIGURE 7.3 LECH3/LECH4 /186/

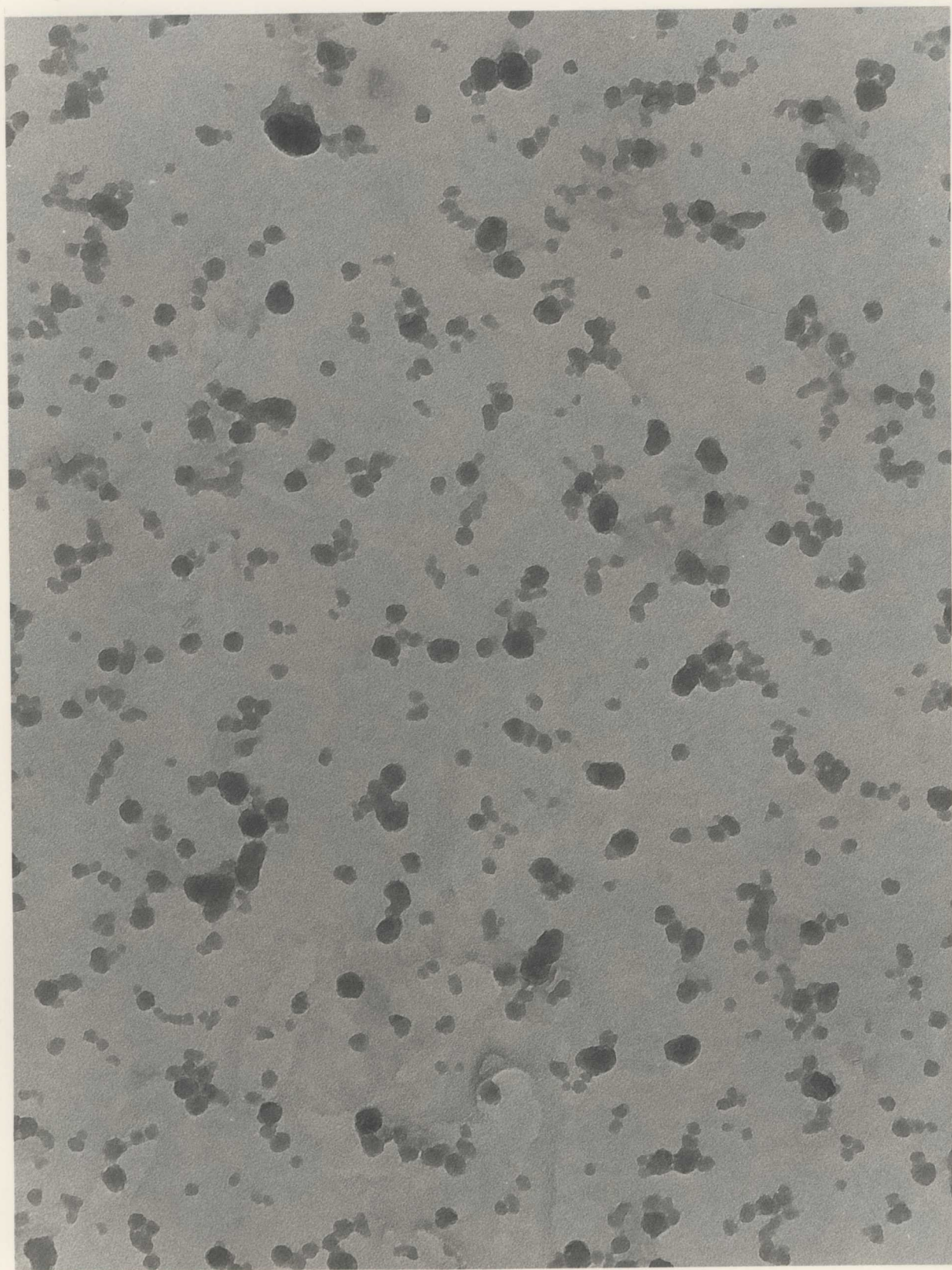


FIGURE 7.4 LECH5 /186/

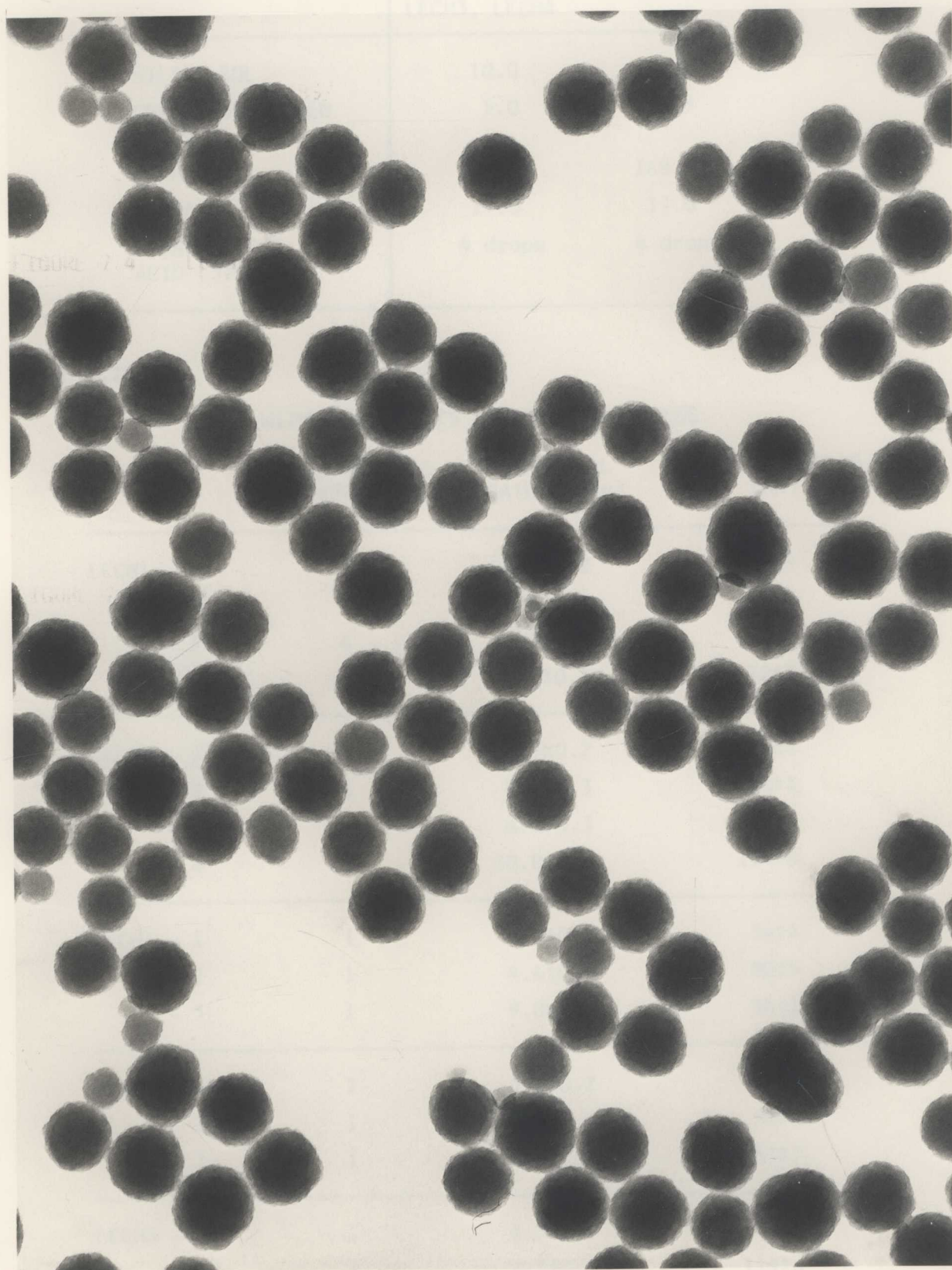


TABLE 7.1a

BATH CONCENTRATIONS

	VOLUME (mls)	
	LECH1, LECH2, LECH3, LECH4	LECH5
SILICA SOL	10.0	7.5
DOUBLY DISTILLED WATER	5.0	7.5
ETHANOL	168.0	168.0
METHANOL	17.0	17.0
HYDROCHLORIC ACID (37%)	4 drops	4 drops

TABLE 7.1b

WITHDRAWAL RATES AND FILM THICKNESS

SAMPLE	No. OF WITHDRAWALS	WITHDRAWAL RATE (mm/s)	FILM THICKNESS (nm)
LECH1 - 1	2	4.0±0.2	25±5
- 2	4	4.0±0.2	47±3
- 3	6	4.0±0.2	72±7
- 4	8	4.0±0.2	72±3
LECH2 - 1	1	2.9±0.2	90±4
- 2	1	4.8±0.3	98±4
- 3	1	6.2±0.3	106±6
- 4	1	10.0±0.5	134±6
LECH3 - 1	1	3.0±0.2	74±4
- 2	1	4.6±0.2	80±5
- 3	1	9.0±0.4	84±10
LECH4 - 1	1	3.0±0.2	72±4
- 2	1	4.6±0.2	92±4
- 3	1	5.9±0.3	153±7
LECH5 - 1	1	2.9±0.2	90±10
- 2	1	3.3±0.2	114±6
- 3	1	4.0±0.3	118±4
- 4	1	4.6±0.3	130±4
- 5	1	6.2±0.3	180±10
- 6	2	3.0±0.2	180±10

REFLECTANCE (%) OF COLLOIDAL SILICA COATINGS ON GLASS

WAVELENGTH (nm)	LECH1				LECH2				LECH3			LECH4			LECH5					
	-1	-2	-3	-4	-1	-2	-3	-4	-1	-2	-3	-1	-2	-3	-1	-2	-3	-4	-5	-6
360	5.44	6.15	8.09	9.03	4.47	4.90	5.44	5.75	3.84	2.31	7.23	1.59	1.59	5.06	3.29	4.42	6.36	6.86	4.11	3.70
400	4.93	5.25	7.29	9.09	3.81	3.99	4.51	5.14	2.97	2.22	6.39	1.47	1.47	4.46	2.56	3.22	6.79	6.69	6.20	5.16
450	4.58	4.43	5.98	8.33	2.83	2.98	3.21	4.67	2.41	2.08	4.95	1.37	1.37	3.84	1.73	6.07	1.54	7.79	6.30	6.45
500	4.61	4.11	5.00	7.36	2.08	2.26	2.22	4.19	2.28	1.81	3.68	1.42	1.27	3.12	1.23	5.21	1.25	8.34	5.54	6.91
550	4.76	4.08	4.34	6.39	1.59	1.80	1.62	3.61	2.39	2.08	2.67	1.57	1.28	2.25	1.00	4.14	0.83	7.86	4.50	6.54
600	4.99	4.16	3.94	5.59	1.39	1.58	1.36	3.00	2.67	2.42	2.08	1.85	1.45	1.54	1.03	3.08	0.71	6.79	3.43	5.64
650	5.20	4.31	3.79	5.04	1.39	1.54	1.33	2.53	2.99	2.73	1.79	2.16	1.69	1.00	1.18	2.20	0.78	4.32	1.87	3.62
700	5.39	4.50	3.78	4.76	1.50	1.63	1.43	2.23	3.36	3.03	1.75	2.53	1.98	0.66	1.42	1.63	0.97	4.32	1.87	3.62
800	5.33	4.46	3.62	4.27	1.89	1.82	1.74	1.46	3.65	3.24	1.94	2.88	2.31	0.57	2.08	0.71	1.49	1.94	0.73	1.63
900	5.72	4.93	4.10	4.34	2.54	2.38	2.37	1.59							2.72	0.64	2.19	0.78	0.64	0.72
1000	6.05	5.33	4.53	4.61	3.15	2.97	2.99	1.97							3.37	0.93	2.86	0.37	0.92	0.40
1100	6.29	5.64	4.90	4.88	3.66	3.46	3.52	2.35							3.92	1.31	3.41	0.34	1.29	0.45
1200	6.51	5.91	5.24	5.16	4.17	3.98	4.01	2.81							4.40	1.80	3.97	0.53	1.76	0.69
1500	6.90	6.49	5.97	5.85	5.22	5.05	5.12	4.07							5.41	3.20	5.17	1.74	3.14	1.94
2000	7.27	7.01	6.71	6.56	6.23	6.08	6.13	5.40							6.36	4.83	6.16	3.66	4.81	3.85
2500	7.37	7.20	6.98	6.86	6.66	6.51	6.56	5.99							6.76	5.64	6.57	4.79	5.58	4.86

TABLE 7.3

COMPARISONS OF CORNING 2947 TRANSMITTANCE VERSUS REFLECTANCE

WAVELENGTH (nm)	REFLECTANCE (%)	TRANSMITTANCE (%)	ABSORPTANCE (%)
360	6.8	90.8	2.4
400	6.8	92.4	0.8
450	6.8	92.5	0.7
500	6.8	92.6	0.6
550	7.0	92.6	0.4
600	7.1	92.4	0.5
650	7.1	92.2	0.7
700	7.5	92.1	0.7
800	7.4	91.8	0.4
900	7.2	92.1	0.7
1000	7.6	91.8	0.6
1100	7.6	91.6	0.8
1200	7.7	91.7	0.6
1500	7.5	92.0	0.5
2000	7.7	92.0	0.3
2500	8.0	91.4	0.6

TABLE 7.4

TRANSMITTANCE (%) OF COLLOIDAL SILICA COATINGS ON GLASS

WAVELENGTH (nm)	LECH1				LECH2				LECH3			LECH4			LECH5					
	-1	-2	-3	-4	-1	-2	-3	-4	-1	-2	-3	-1	-2	-3	-1	-2	-3	-4	-5	-6
360	91.9	90.8	89.8	90.0	93.7	92.9	90.9	91.9	94.1	92.7	91.0	94.0	94.2	91.8	94.5	93.4	90.8	90.6	92.9	92.9
400	94.4	93.6	92.1	91.5	95.8	95.2	93.9	94.8	95.4	94.9	92.3	95.6	96.3	94.0	97.0	96.4	93.3	93.2	93.2	93.8
450	95.0	94.6	93.2	92.1	96.4	96.1	95.1	95.2	96.0	95.5	92.8	95.9	96.9	95.0	97.7	97.5	94.2	94.2	92.5	93.4
500	95.2	95.1	94.2	93.0	96.9	96.7	96.0	95.5	96.1	96.2	94.4	96.2	97.5	96.2	98.0	98.1	95.1	95.1	92.4	93.4
550	95.2	95.5	94.8	93.9	97.3	97.1	96.7	96.0	96.5	96.5	95.8	96.2	97.8	97.3	98.2	98.5	96.1	96.2	93.1	93.9
600	95.0	95.4	95.1	94.4	97.4	97.1	97.0	96.3	96.3	96.5	96.4	96.1	97.6	98.1	98.0	98.5	96.9	97.0	93.9	94.6
650	94.8	95.4	95.3	94.9	97.4	97.1	97.0	96.7	95.6	96.0	96.8	95.6	97.1	98.2	97.9	98.4	97.6	97.7	95.1	95.5
700	94.5	95.1	95.2	95.0	97.1	96.9	96.9	96.8	95.4	95.7	97.1	95.2	96.6	98.4	97.5	98.1	98.0	98.1	96.1	96.3
800	93.9	94.4	94.8	94.9	96.3	96.1	96.3	96.8	94.6	95.1	97.0	94.2	95.9	98.5	96.5	97.2	98.3	98.3	97.4	97.5
900	93.6	93.4	94.4	95.2	96.4	96.3	96.0	97.2	93.7	94.5	96.8	93.8	95.0	97.5	96.3	96.1	95.5	98.3	98.1	97.9
1000	93.2	93.1	93.9	94.9	95.7	95.8	95.5	97.3	93.1	93.9	96.4	93.3	94.4	96.8	95.4	95.6	98.1	98.1	98.8	98.1
1100	92.8	92.9	93.7	94.6	95.2	95.2	94.9	96.7	92.8	93.7	96.2	93.1	94.0	96.4	95.0	95.1	97.7	97.3	98.5	98.1
1200	92.6	92.9	93.4	94.2	94.9	94.7	94.3	96.1	92.8	93.3	95.8	92.8	93.8	96.1	94.3	94.6	97.3	96.9	98.6	98.1
1500	92.9	93.0	93.3	93.9	94.3	94.2	94.0	95.6	92.6	93.2	95.1	92.9	93.4	95.3	94.1	93.9	96.2	96.0	97.9	97.2
2000	92.8	92.7	92.9	93.4	93.5	93.4	93.1	94.4	92.3	92.7	94.0	93.4	92.9	93.8	93.1	93.2	94.6	94.8	95.9	95.3
2500	92.6	92.1	92.2	92.6	93.0	92.8	92.1	93.2	91.7	92.0	93.0	91.7	91.9	92.8	92.6	92.5	93.5	93.3	94.4	93.8

TABLE 7.5

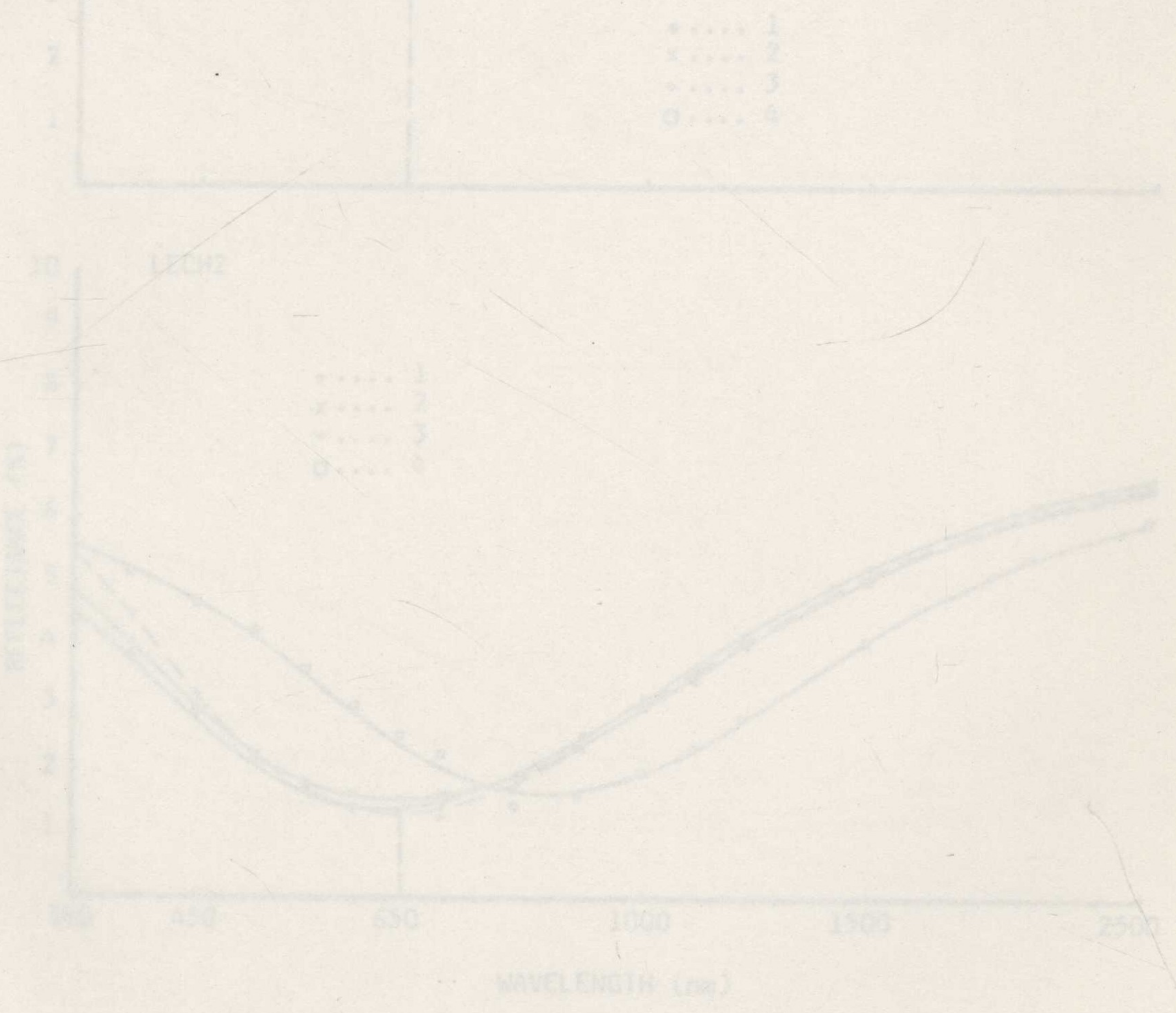
SOLAR TRANSMITTANCE									
WAVELENGTH (nm)	AIR MASS (1) G	LECH1 - 3		LECH2 - 1		LECH4 - 3		LECH5 - 2	
		T	G	T	G	T	G	T	G
360	513.7	89.8	461.3	93.7	481.3	91.8	471.6	93.4	479.8
400	849.9	92.1	782.8	95.8	814.2	94.0	798.9	96.4	819.3
450	1388.4	93.2	1294.0	96.4	1338.4	95.0	1319.0	97.5	1353.7
500	1451.2	94.2	1367.0	96.9	1406.2	96.2	1396.1	98.1	1423.6
550	1336.6	94.8	1267.1	97.3	1300.5	97.3	1300.5	98.5	1316.6
600	1660.0	95.1	1578.7	97.4	1616.8	98.1	1628.5	98.5	1635.1
650	1511.0	95.3	1440.0	97.4	1471.7	98.2	1483.8	98.4	1486.8
700	1175.3	95.2	1118.9	97.1	1141.2	98.4	1156.5	98.1	1153.0
800	981.2	94.8	930.2	96.3	944.9	98.5	966.5	97.2	953.7
900	448.9	94.4	423.8	96.4	432.7	97.5	437.7	96.1	431.4
1000	580	93.9	544.6	95.7	555.1	96.8	561.4	95.6	554.5
1100	504.8	93.7	473.0	95.2	480.6	96.4	486.6	95.1	483.1
1200	424.0	93.4	396.0	94.9	402.4	96.1	407.5	94.6	401.1
1500	216.0	93.3	201.5	94.3	203.7	95.3	205.8	93.9	202.8
2000	69.0	92.9	64.1	93.5	64.5	93.8	64.7	93.2	64.3
2500	20.0	92.2	18.4	93.0	18.6	92.8	18.6	92.5	18.5
SOLAR TRANSMITTANCE (%)		94.5±0.3		96.5±0.3		96.8±0.3		97.3±0.3	

T denotes TRANSMITTANCE
G denotes AMOUNT OF SOLAR FLUX TRANSMITTED

TABLE 7.6

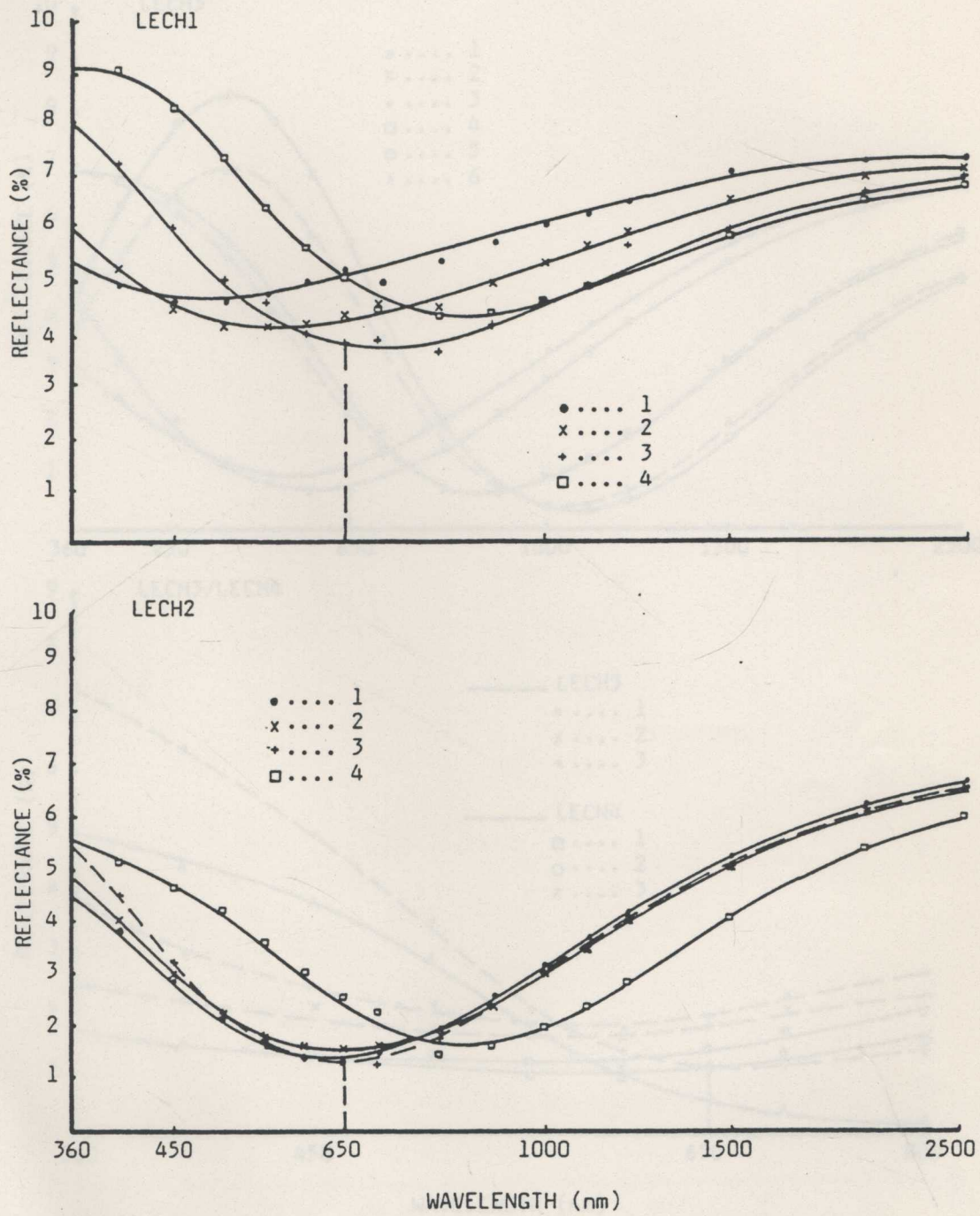
REFRACTIVE INDEX, REFLECTANCE MINIMA, DENSITY AND PARTICLE SIZE OF THE SILICA FILMS

SAMPLE	PARTICLE SIZE (nm)	REFLECTANCE MINIMA (%) (AT 650 nm)	REFRACTIVE INDEX (AT 650 nm) (0.002)	DENSITY (g/cm ³)
LECH1 - 3	5±2	3.6±0.2	1.450	1.67±0.23
LECH2 - 1	16±3	1.3±0.1	1.355	1.58±0.26
LECH3 - 3	22±6	1.0±0.1		1.44±0.28
LECH4 - 3	22±6	0.5±0.1	1.309	1.26±0.34
LECH5 - 2	75±9	0.8±0.2	1.153	1.17±0.34



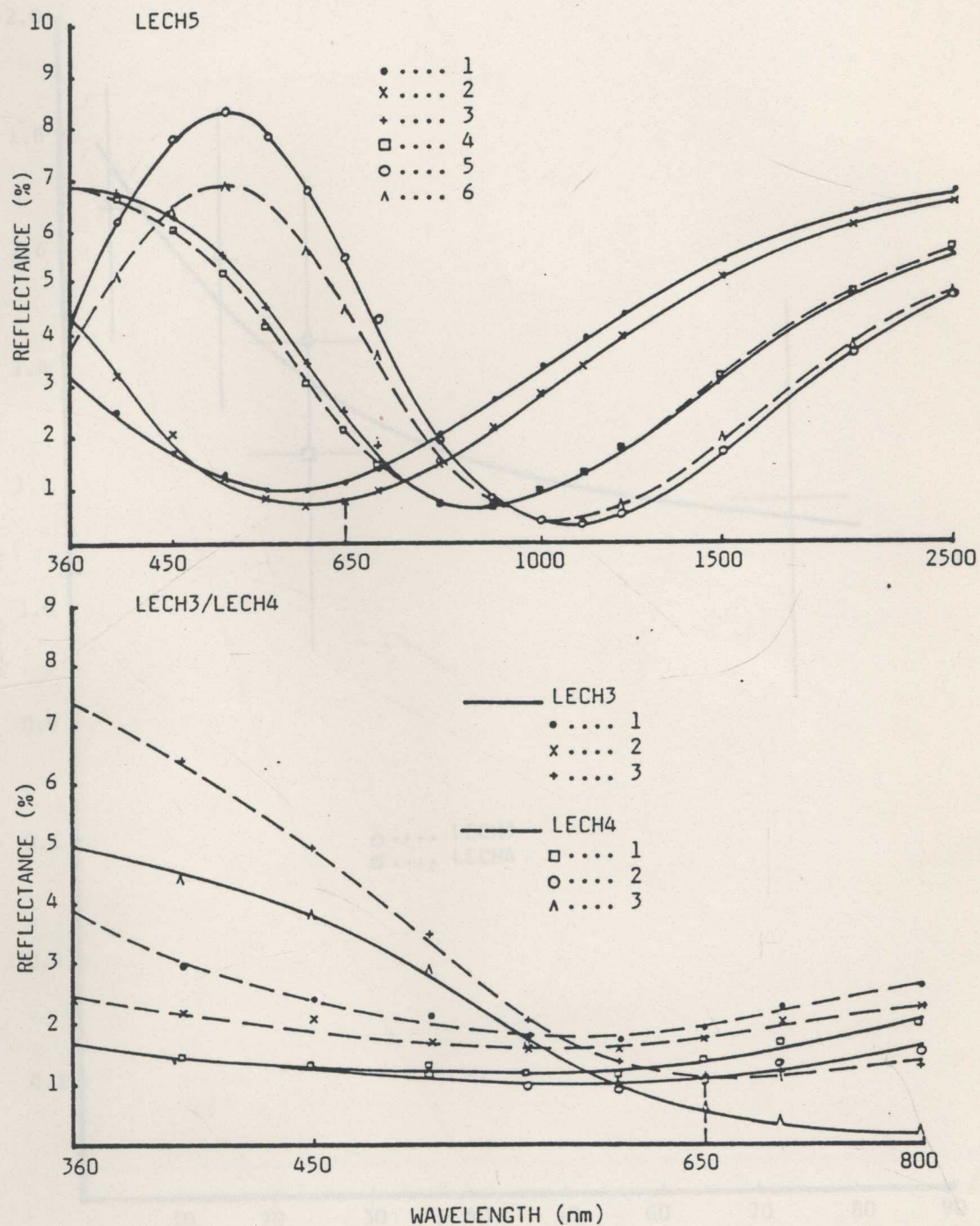
GRAPH 7.1a

REFLECTANCE OF COATINGS ON GLASS VERSUS WAVELENGTH



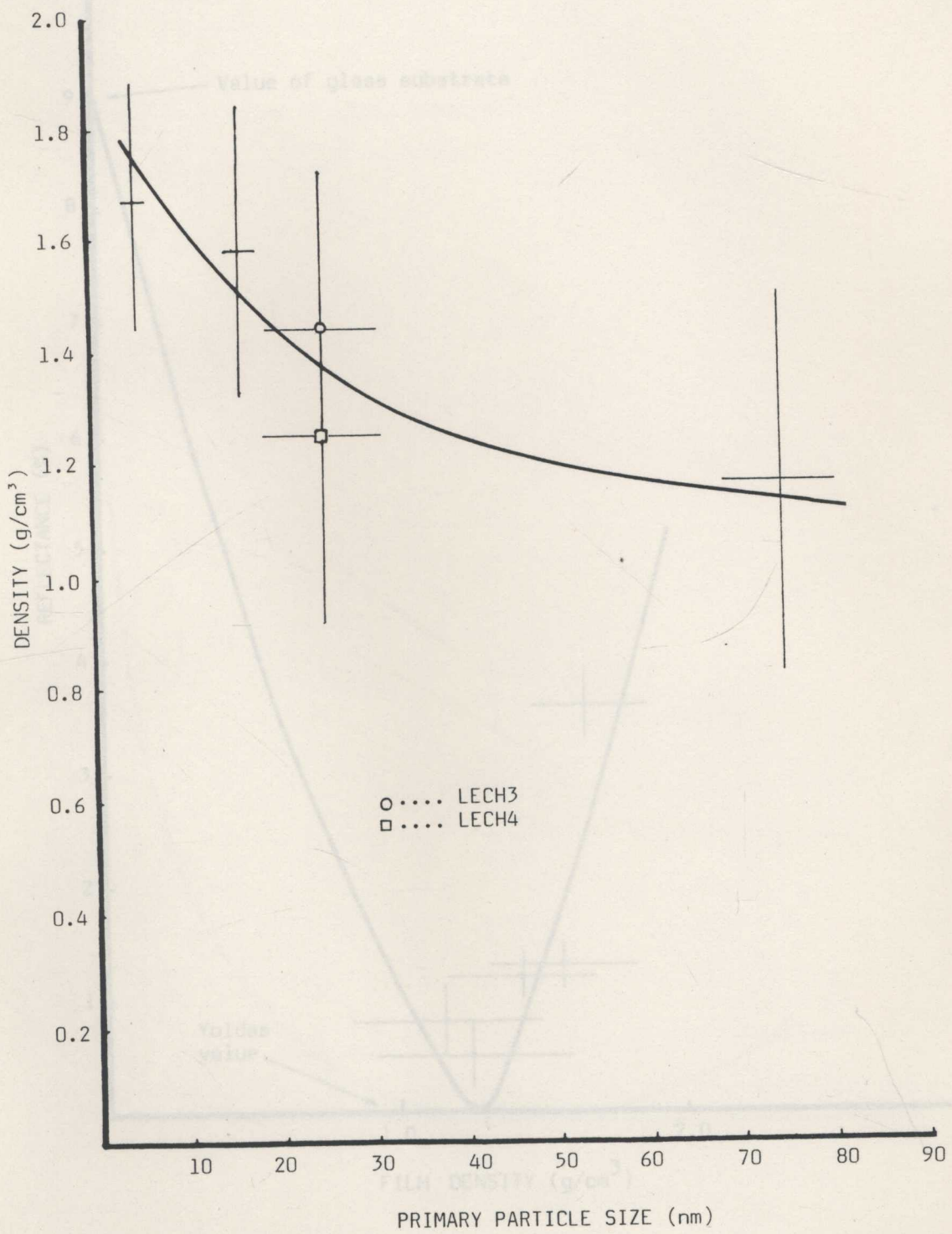
GRAPH 7.1b

REFLECTANCE OF COATINGS ON GLASS VERSUS WAVELENGTH



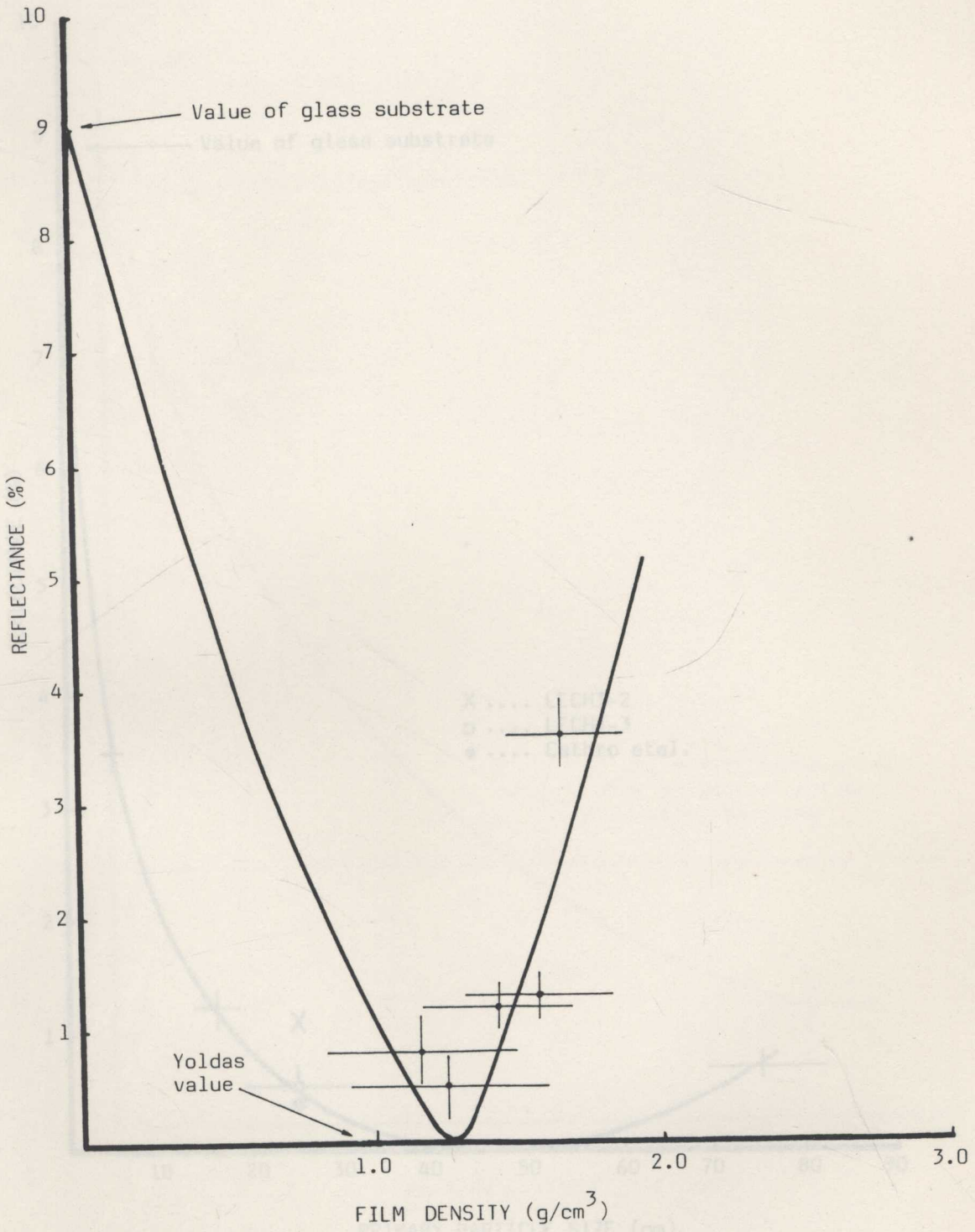
GRAPH 7.2

FILM DENSITY VERSUS SILICA PRIMARY PARTICLE SIZE



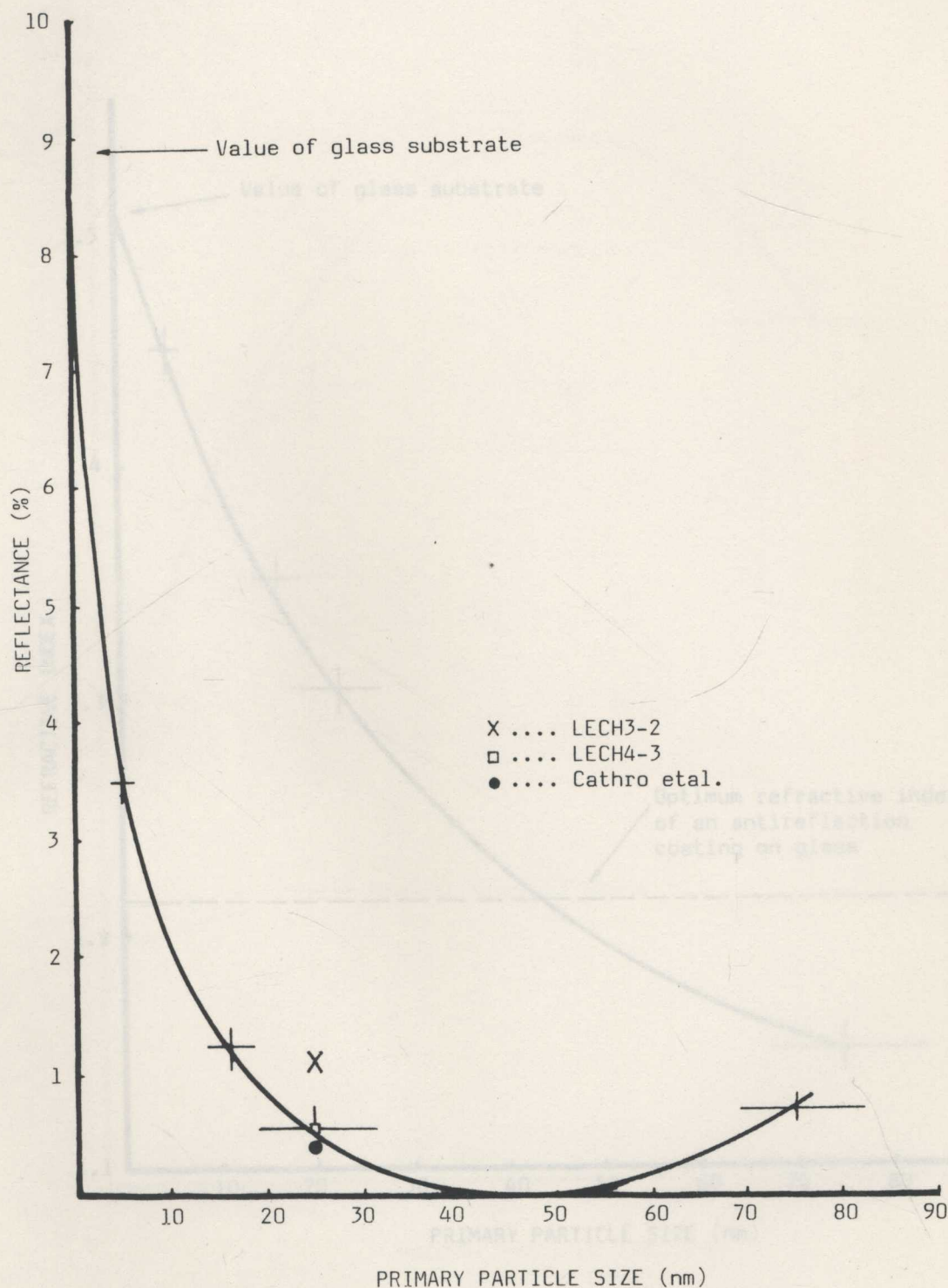
GRAPH 7.3

MINIMUM REFLECTANCE AT 650 nm
VERSUS DENSITY



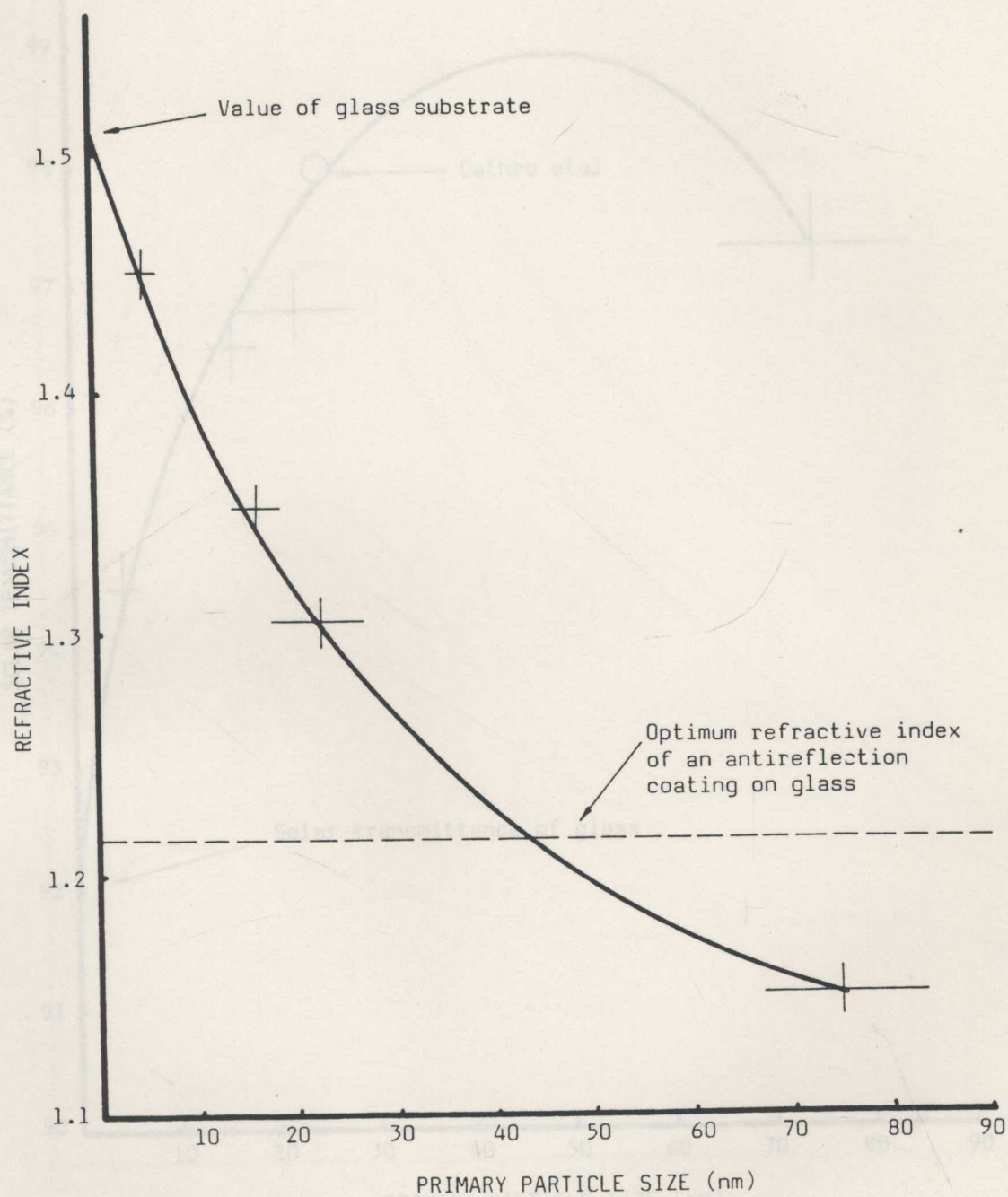
GRAPH 7.4

MINIMUM REFLECTANCE AT 650 nm VERSUS
SILICA PRIMARY PARTICLE SIZE



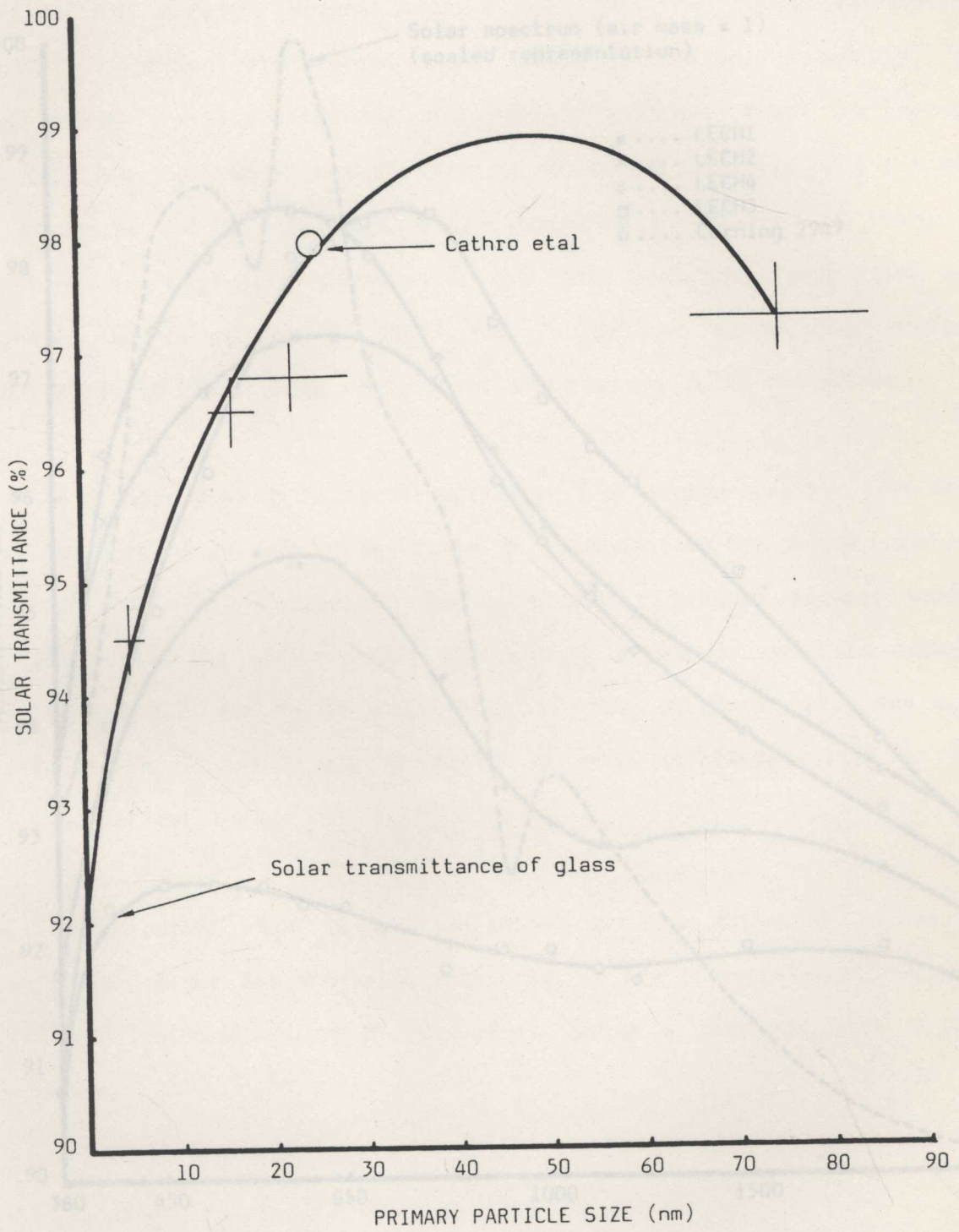
GRAPH 7.5

REFRACTIVE INDEX (AT 650 nm) VERSUS
SILICA PRIMARY PARTICLE SIZE



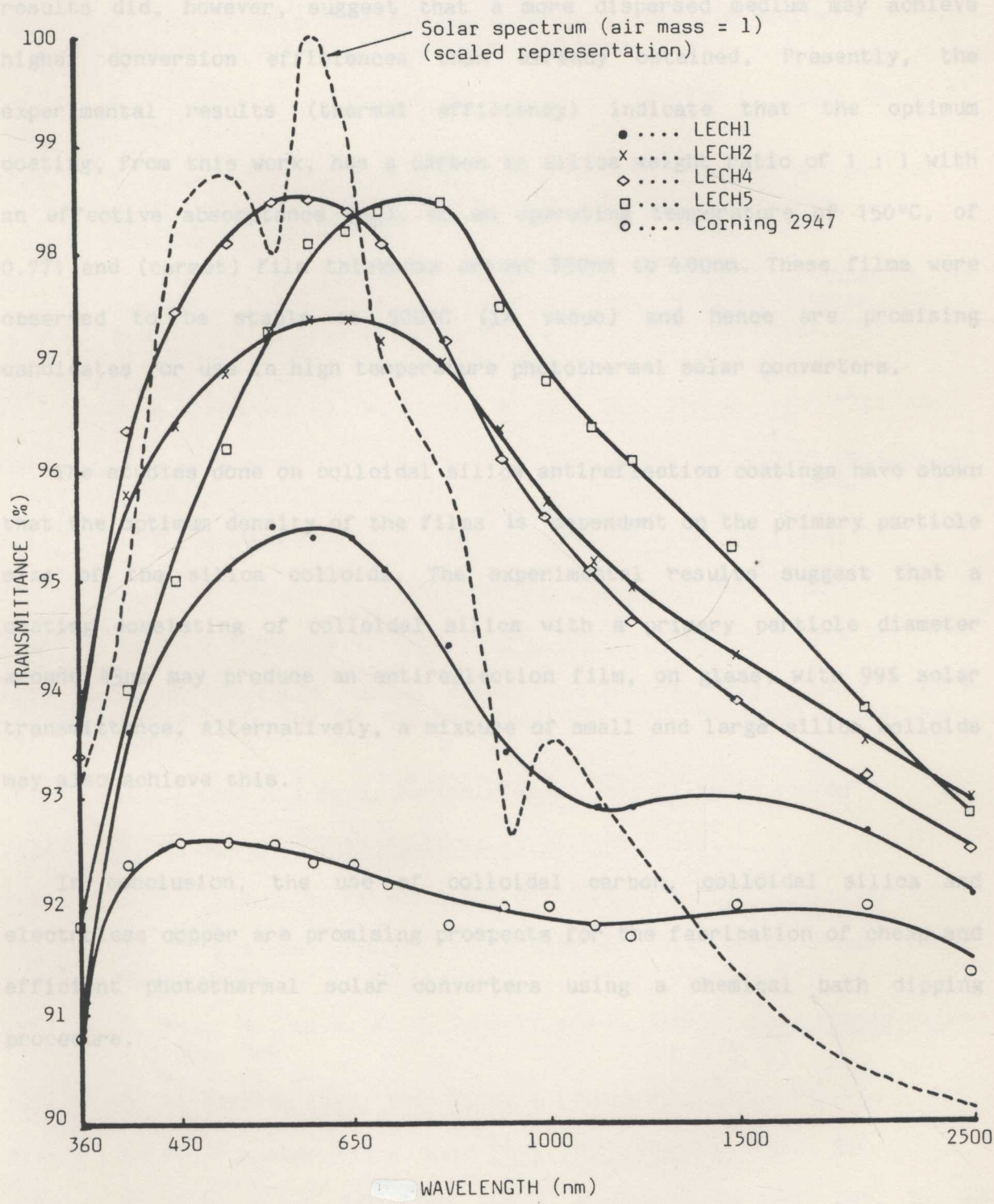
GRAPH 7.6

SOLAR TRANSMITTANCE VERSUS SILICA PARTICLE SIZE



GRAPH 7.7

TRANSMITTANCE THROUGH COATINGS VERSUS WAVELENGTH



CONCLUSION

It was found that the Maxwell Garnett equation did not describe the mixed colloidal carbon and silica cermet used in this work. The theoretical results did, however, suggest that a more dispersed medium may achieve higher conversion efficiencies than already obtained. Presently, the experimental results (thermal efficiency) indicate that the optimum coating, from this work, has a carbon to silica weight ratio of 1 : 1 with an effective absorptance (a_m), at an operating temperature of 150°C, of 0.771 and (cermet) film thickness around 350nm to 400nm. These films were observed to be stable at 500°C (in vacuo) and hence are promising candidates for use in high temperature photothermal solar converters.

The studies done on colloidal silica antireflection coatings have shown that the optimum density of the films is dependent on the primary particle size of the silica colloids. The experimental results suggest that a coating consisting of colloidal silica with a primary particle diameter around 45nm may produce an antireflection film, on glass, with 99% solar transmittance. Alternatively, a mixture of small and large silica colloids may also achieve this.

In conclusion, the use of colloidal carbon, colloidal silica and electroless copper are promising prospects for the fabrication of cheap and efficient photothermal solar converters using a chemical bath dipping procedure.

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- APPENDIX A
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 - /186/ Aqueous sol on carbon coated copper grid. Samples examined on a Philips EM 400, operating at 100 kV.

TOTAL FRONT REFLECTANCE (%) ON GLASS

WAVELENGTH (nm)	KITZ1					KITZ2					KITZ3					KITZ4				
	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5
360	5.99	4.68	3.68	2.95	2.60	4.88	3.37	2.66	2.39	2.18	5.46	3.52	2.74	2.30	1.96	4.76	3.35	2.69	2.41	2.28
400	6.14	4.76	3.77	3.00	2.64	5.19	3.61	2.85	2.55	2.32	5.80	3.75	2.91	2.44	2.06	4.82	3.39	2.72	2.43	2.29
450	6.29	4.91	3.95	3.14	2.74	5.48	3.87	3.09	2.73	2.47	6.06	3.97	3.11	2.61	2.18	4.96	3.52	2.83	2.50	2.37
500	6.40	5.10	4.13	3.29	2.84	5.65	4.03	3.22	2.84	2.54	6.20	4.10	3.20	2.68	2.22	5.12	3.64	2.89	2.56	2.40
550	6.52	5.31	4.24	3.44	2.98	5.82	4.20	3.40	2.96	2.62	6.32	4.23	3.34	2.80	2.30	5.38	3.87	3.12	2.72	2.54
600	6.52	5.49	4.53	3.60	3.12	5.98	4.41	3.59	3.13	2.74	6.43	4.37	3.50	2.92	2.40	5.57	4.06	3.31	2.85	2.66
650	6.59	5.64	4.70	3.73	3.25	6.13	4.62	3.76	3.30	2.86	6.54	4.51	3.64	3.06	2.51	5.79	4.28	3.50	3.02	2.88
700	6.62	5.79	4.88	3.88	3.39	6.21	4.78	3.92	3.42	2.95	6.57	4.60	3.73	3.16	2.60	5.89	4.44	3.66	3.15	2.89
800	6.55	6.01	5.12	4.09	3.47	6.39	5.23	4.21	3.61	3.10	6.68	4.81	3.93	3.37	2.74	5.60	3.72	2.82	2.09	1.94
900	6.66	6.29	5.56	4.47	3.82	6.56	5.60	4.63	4.01	3.32	6.79	5.09	4.22	3.64	2.99	5.75	4.22	3.24	2.36	2.18
1000	6.79	6.59	5.93	4.87	4.19	6.75	5.97	5.07	4.46	3.70	6.94	5.42	4.60	4.07	3.35	6.08	4.74	3.78	2.95	2.59
1100	6.94	6.77	6.23	5.22	4.59	6.88	6.28	5.49	4.82	4.04	7.02	5.71	4.87	4.37	3.63	6.20	5.29	4.33	3.38	3.07
1200	6.95	6.96	6.56	5.60	4.97	6.96	6.59	5.87	5.25	4.37	7.13	5.98	5.24	4.69	4.00	6.44	5.82	4.82	3.90	3.64
1500	7.18	7.43	7.24	6.70	5.90	7.37	7.29	6.94	6.35	5.44	7.40	6.77	6.11	5.68	4.95	6.87	6.88	6.03	5.29	5.04
2000	7.38	7.70	7.82	7.88	7.32	7.60	7.86	7.76	7.76	6.95	7.60	7.52	7.24	6.96	6.59	7.00	7.42	7.06	6.94	7.00
2500	7.50	7.80	8.03	8.46	8.16	7.70	8.12	8.35	8.52	8.02	7.66	7.94	8.01	7.96	7.97	6.91	8.14	8.04	7.92	8.63

TOTAL BACK REFLECTANCE (%) ON GLASS

WAVELENGTH (nm)	KITZ1					KITZ2					KITZ3					KITZ4				
	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5
360	8.59	7.83	7.73	7.58	7.65	7.88	8.04	8.06	8.11	8.16	8.19	8.26	8.26	8.16	8.13	8.74	8.74	9.05	9.08	9.02
400	8.12	7.36	7.30	7.22	7.23	7.80	7.55	7.55	7.55	8.05	8.16	8.21	8.16	8.05	8.00	8.14	8.14	8.42	8.47	8.39
450	7.54	6.89	6.81	6.75	6.75	7.36	7.62	7.64	7.63	7.67	7.80	7.85	7.77	7.65	7.56	7.49	7.49	7.76	7.77	7.64
500	7.15	6.56	6.51	6.44	6.44	6.85	7.18	7.19	7.18	7.15	7.37	7.40	7.32	7.19	7.10	6.91	6.98	7.20	7.22	7.08
550	6.84	6.31	6.35	6.23	6.23	6.45	6.83	6.87	6.82	6.82	7.01	7.05	6.97	6.86	6.75	6.59	6.70	6.92	6.96	6.82
600	6.60	6.09	6.07	6.07	6.07	6.13	6.53	6.60	6.59	6.56	6.73	6.77	6.70	6.60	6.47	6.27	6.44	6.68	6.70	6.58
650	6.51	5.92	5.92	5.92	5.92	5.89	6.29	6.42	6.42	6.35	6.52	6.53	6.46	6.39	6.28	6.03	6.22	6.45	6.53	6.39
700	6.32	5.78	5.78	5.37	5.37	5.73	6.10	6.25	6.27	6.20	6.33	6.34	6.29	6.20	6.09	5.80	6.04	6.26	6.38	5.94
800	5.97	5.06	5.40	5.54	5.11	5.37	5.58	5.81	5.85	5.83	6.01	5.91	5.86	5.83	5.71	4.95	5.86	6.01	6.07	6.16
900	5.93	4.97	5.28	5.48	5.09	5.30	5.31	5.57	5.68	5.67	5.88	5.69	5.63	5.63	5.57	4.71	5.49	5.74	5.78	5.95
1000	5.91	4.93	5.20	5.46	5.08	5.30	5.20	5.47	5.66	5.60	5.86	5.59	5.49	5.55	5.54	4.71	5.32	5.60	5.73	5.77
1100	5.93	4.94	5.11	5.46	5.10	5.36	5.11	5.37	5.72	5.59	5.86	5.51	5.45	5.46	5.51	4.70	5.23	5.58	5.82	5.82
1200	5.99	4.96	5.12	5.46	5.15	5.44	5.08	5.32	5.69	5.55	5.91	5.49	5.43	5.45	5.52	4.66	5.11	5.52	5.77	5.77
1500	6.19	5.11	5.17	5.48	5.29	5.70	5.12	5.22	5.59	5.58	6.08	5.48	5.43	5.46	5.87	4.81	5.04	5.42	5.81	5.87
2000	6.49	5.44	5.36	5.59	5.40	6.07	5.37	5.27	5.62	5.63	6.34	5.58	5.60	5.68	5.89	4.94	5.15	5.43	5.85	5.92
2500	6.68	5.58	5.42	5.66	5.42	6.30	5.61	5.42	5.69	5.76	6.56	5.75	5.84	5.97	6.21	5.33	5.46	5.59	6.06	6.32

DIFFUSE FRONT REFLECTANCE (%) ON GLASS

WAVELENGTH (nm)	KITZ1					KITZ2					KITZ3					KITZ4				
	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5
360	2.20	2.69	2.80	2.73	2.69	2.21	2.55	2.55	2.49	2.41	2.07	2.72	2.57	2.41	2.20	2.35	2.41	2.40	2.29	2.20
400	2.03	2.59	2.76	2.74	2.68	2.04	2.46	2.52	2.47	2.39	1.97	2.71	2.58	2.41	2.20	2.19	2.35	2.35	2.24	2.19
450	1.75	2.40	2.70	2.80	2.74	1.81	2.39	2.50	2.50	2.43	1.80	2.70	2.62	2.47	2.21	2.03	2.33	2.33	2.25	2.22
500	1.50	2.21	2.57	2.76	2.74	1.56	2.26	2.47	2.50	2.42	1.61	2.65	2.61	2.47	2.22	1.77	2.24	2.30	2.35	2.19
550	1.28	2.01	2.48	2.77	2.77	1.39	2.16	2.45	2.52	2.45	1.45	2.65	2.66	2.54	2.27	1.65	2.24	2.34	2.26	2.24
600	1.09	1.86	2.35	2.79	2.81	0.72	2.07	2.41	2.55	2.48	1.30	2.62	2.71	2.60	2.35	1.50	2.18	2.35	2.27	2.27
650	0.85	1.60	2.13	2.70	2.75	0.58	1.94	2.37	2.55	2.50	1.19	2.58	2.72	2.64	2.40	1.37	2.10	2.33	2.31	2.38
700	0.75	1.46	2.01	2.67	2.76	0.47	1.84	2.32	2.55	2.52	1.07	2.51	2.71	2.69	2.45	1.24	2.03	2.32	2.30	2.31
800	0.45	1.02	1.53	2.46	2.68	0.67	1.42	1.99	2.33	2.37	0.45	1.82	2.14	2.13	2.17	0.25	0.87	1.35	1.05	1.10
900	0.30	0.83	1.27	2.30	2.63	0.53	1.20	1.83	2.28	2.36	0.37	1.69	2.14	2.22	2.32	0.32	0.79	1.32	1.09	1.14
1000	0.16	0.70	1.10	2.19	2.71	0.48	1.08	1.66	2.25	2.41	0.34	1.64	2.23	2.35	2.51	0.21	0.68	1.16	1.07	1.15
1100	0.20	0.60	0.97	2.04	2.66	0.43	0.95	1.53	2.14	2.38	0.30	1.51	2.23	2.43	2.68	0.21	0.60	1.06	1.10	1.22
1200	0.15	0.50	0.84	1.87	2.59	0.37	0.83	1.36	2.05	2.36	0.28	1.41	2.23	2.51	2.82	0.21	0.51	1.05	1.10	1.30
1500	0.11	0.36	0.57	1.43	2.23	0.35	0.61	1.01	1.64	2.07	0.27	1.08	2.06	2.38	3.29	0.22	0.35	0.79	0.85	1.20
2000	0.06	0.21	0.38	0.95	1.63	0.25	0.46	0.70	1.19	1.64	0.15	0.61	1.47	2.33	3.23	0.12	0.16	0.42	0.42	0.79
2500	0.06	0.16	0.27	0.66	1.20	0.26	0.38	0.50	0.89	1.12	0.13	0.45	1.02	1.78	2.95	0.08	0.02	0.31	0.24	0.44
2500	0.00	0.23	0.36	0.95	1.24	0.25	0.47	0.77	1.17	1.14	0.10	0.61	1.13	1.28	1.13	0.09	0.02	0.32	0.43	0.32

DIFFUSE BACK REFLECTANCE (%) ON GLASS

WAVELENGTH (nm)	KITZ1					KITZ2					KITZ3					KITZ4				
	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5	-1	-2	-3	-4	-5
360	1.01	1.10	1.06	0.97	0.87	1.00	0.91	0.79	0.70	0.69	0.88	0.88	0.77	0.67	0.57	0.97	0.79	0.69	0.61	0.56
400	1.06	1.13	1.06	0.95	0.83	1.03	0.93	0.78	0.67	0.67	0.97	0.92	0.78	0.66	0.53	1.01	0.81	0.66	0.52	0.48
450	1.07	1.11	1.04	0.90	0.77	1.06	0.94	0.79	0.66	0.61	1.02	0.96	0.78	0.62	0.48	1.07	0.82	0.65	0.49	0.43
500	1.04	1.15	1.05	0.88	0.73	1.03	0.97	0.78	0.64	0.56	1.04	0.96	0.76	0.60	0.42	1.00	0.74	0.52	0.36	0.29
550	0.97	1.16	1.07	0.89	0.71	1.01	1.00	0.79	0.66	0.54	1.05	1.00	0.79	0.59	0.40	1.11	0.87	0.64	0.47	0.38
600	0.90	1.16	1.09	0.90	0.72	0.98	1.03	0.82	0.68	0.53	1.05	1.03	0.80	0.60	0.38	1.10	0.90	0.66	0.46	0.37
650	0.73	1.05	1.00	0.83	0.63	0.91	1.03	0.84	0.68	0.51	1.01	1.04	0.82	0.61	0.37	1.07	0.93	0.67	0.48	0.37
700	0.67	1.03	1.02	0.86	0.65	0.86	1.03	0.86	0.71	0.50	0.97	1.06	0.83	0.62	0.37	1.05	0.95	0.69	0.47	0.52
800	0.49	0.89	0.98	0.89	0.70	0.67	0.92	0.83	0.67	0.47	0.46	0.62	0.46	0.36	0.26	0.38	0.31	0.24	0.04	0.04
900	0.39	0.82	0.94	0.94	0.73	0.57	0.88	0.83	0.69	0.49	0.37	0.65	0.50	0.37	0.27	0.32	0.38	0.27	0.12	0.14
1000	0.32	0.78	0.93	0.99	0.82	0.55	0.91	0.90	0.80	0.55	0.36	0.73	0.58	0.44	0.30	0.21	0.35	0.29	0.13	0.16
1100	0.25	0.72	0.90	1.06	0.90	0.50	0.89	0.95	0.88	0.61	0.33	0.78	0.65	0.50	0.34	0.21	0.37	0.30	0.30	0.15
1200	0.20	0.66	0.87	1.14	0.96	0.45	0.86	0.97	0.95	0.65	0.32	0.87	0.74	0.48	0.41	0.22	0.36	0.36	0.19	0.18
1500	0.13	0.52	0.79	1.26	1.18	0.37	0.89	1.03	1.14	0.86	0.28	0.98	0.98	0.80	0.59	0.22	0.34	0.46	0.26	0.24
2000	0.05	0.35	0.58	1.21	1.33	0.31	0.64	0.99	1.31	1.14	0.13	0.80	1.15	1.06	0.84	0.12	0.17	0.42	0.33	0.19
2500	0.00	0.23	0.36	0.95	1.24	0.25	0.47	0.77	1.17	1.14	0.10	0.61	1.13	1.28	1.13	0.09	0.02	0.32	0.43	0.32