

Material Science

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Chapter 17. Optical properties

Engineering materials are important in everyday life because of their versatile structural properties. Other than these properties, they do play an important role because of their physical properties. Prime physical properties of materials include: electrical properties; thermal properties; magnetic properties; and optical properties. Optical properties play an important role in daily life. They have had a significant impact on the development of the communications infrastructure and the information technology. They are also useful in fields like medicine, manufacturing, astronomy, etc.

The goal of this chapter is to present basic concepts about optical properties, optical properties of metals and non-metals, and finally applications of optical phenomena.

17.1 Basic concepts

Optical property of a material is related to the interaction of it with electromagnetic radiation. This radiation may have characteristics that fall in the visible light spectrum, or may be even out of it. Electromagnetic spectrum of radiation spans the wide range from γ -rays with wavelength as 10^{-12} m, through x-rays, ultraviolet, visible, infrared, and finally radio waves with wavelengths as long as 10^5 m. Visible light is one form of electromagnetic radiation with wavelengths ranging from 0.39 to 0.77 μm . It contains color bands from violet through red, as shown in the *figure 17.1*. White light is simply a mixture of all colors. The ultraviolet region covers the range from about 0.01 to about 0.40 μm , and the infrared region extends from about 0.75 to 1000 μm .

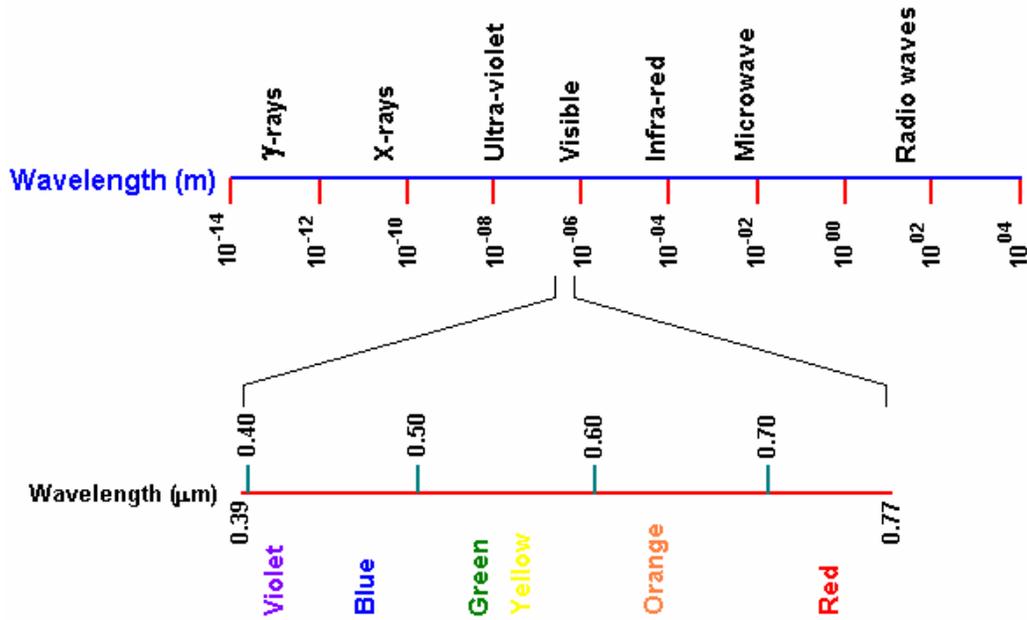


Figure-17.1: Wave length spectrum of electro-magnetic waves.

The true nature of the light will probably never be known. However, light can be considered as having waves and consisting of particles called photons. The important characteristics of the photons are related by the following equation. This equation allows us to consider the photon as a particle of energy, or as a wave with a characteristic wavelength and frequency.

$$E = h\nu = \frac{hc_0}{\lambda}$$

where E – energy, h – Planck’s constant (6.62×10^{-34} J.sec), ν – frequency, c_0 – speed of light in vacuum (3×10^8 m/sec), and λ – wavelength.

All materials interact in some way with light. Interaction of photons with the electronic or crystal structure of a material leads to a number of phenomena. The photons may give their energy to the material (absorption); photons give their energy, but photons of identical energy are immediately emitted by the material (reflection); photons may not interact with the material structure (transmission); or during transmission photons are changes in velocity (refraction).

At any instance of light interaction with a material, the total intensity of the incident light striking a surface is equal to sum of the absorbed, reflected, and transmitted intensities i.e.

$$I_0 = I_A + I_R + I_T$$

The intensity is defined as the number of photons impinging on a surface per unit area per unit time. Materials that are capable of transmitting light with relatively little absorption and reflection are called *transparent materials* i.e. we can see through them. *Translucent materials* are those through which light is transmitted diffusely i.e. objects are not clearly distinguishable when viewed through. Those materials that are impervious to the transmission of visible light are termed as *opaque materials*.

17.2 Optical properties of metals and alloys

Typical characteristic of metals with respect to crystal structure is that they possess a high-energy band that is only partially filled with electrons. When visible light is directed on a metal surface, the energy is used to excite electrons into unoccupied energy states above the Fermi level, thus making metals behave as opaque materials i.e. light is absorbed. Except of thin sections, metals strongly reflect and/or absorb incident radiation for long wavelengths to the middle of the ultraviolet range i.e. metals are opaque to all electromagnetic radiation on the low end of the frequency spectrum, from radio waves, through infrared, visible, into middle of the ultraviolet radiation. However, metals are transparent to high end frequencies, ex. x-ray and γ -ray radiation. Total absorption by metals is within a very thin outer layer, usually less than 0.1 μm ; thus only metallic films thinner than 0.1 μm are capable of transmitting visible light.

Most of the absorbed radiation is emitted from the metallic surface in the form of visible light of the same wavelength as reflected light. The reflectivity of metals is about 0.95, while the rest of impinged energy is dissipated as heat. The amount of energy absorbed by metals depends on the electronic structure of each particular metal. For example: with copper and gold there is greater absorption of the short wavelength colors such as green and blue and a greater reflection of yellow, orange and red wavelengths. Other metals such as silver and aluminium strongly reflect all parts of the visible spectrum and show a white silvery color.

17.3 Optical properties of non-metallic materials

By virtue of their electron structure with characteristic energy band structures, non-metallic materials may be transparent to visible lights. Thus, all four optical phenomena such as absorption, reflection, transmission and refraction are important for these materials.

Refraction: When light photons are transmitted through a material, they causes polarization of the electrons in the material and by interacting with the polarized materials, photons lose some of their energy. As a result of this, the speed of light is reduced and the beam of light changes direction.

The relative velocity of light passing through a medium is expressed by the optical property called the index of refraction (n), and is defined as:

$$n = \frac{c_0}{c}$$

where c_0 – speed of light in vacuum, c – speed of light in the concerned material. If the angle of incidence from a normal to the surface is θ_i , and the angle of refraction is θ_r , the refractive index of the medium, n , is given by

$$n = \frac{\sin \theta_i}{\sin \theta_r}$$

provided that the incident light is coming from a phase of low refractive index such as vacuum or air. Reflection and refraction of light is shown in *figure 17.2*.

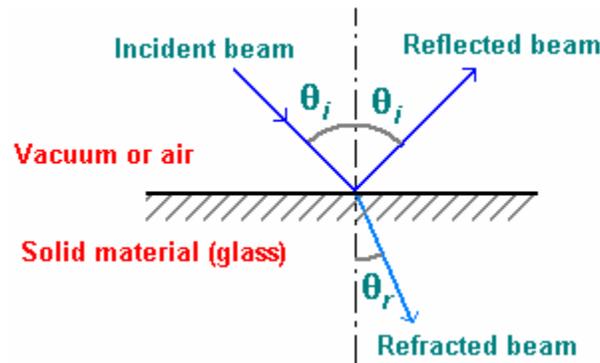


Figure-17.2: Reflection and refraction of light.

The speed of light in a material can be related to its electrical and magnetic properties as:

$$c = \frac{1}{\sqrt{\mu \cdot \epsilon}}$$

where ϵ – electrical permittivity, and μ – magnetic permeability. Thus,

$$n = \frac{c_0}{c} = \frac{\sqrt{\mu \cdot \epsilon}}{\sqrt{\mu_0 \cdot \epsilon_0}} = \sqrt{\mu_r \cdot \epsilon_r}$$

Since most substances are only slightly magnetic i.e. $\mu_r \approx 1$, then

$$n \cong \sqrt{\epsilon_r}$$

Thus, for transparent materials, index of refraction and dielectric constant are related. Refractive indices of some materials are listed in the *table 17.1*.

Table-17.1: Index of refraction for typical materials.

<i>Material</i>	<i>Refractive index</i>	<i>Material</i>	<i>Refractive index</i>
Air	1.00	Epoxy	1.58
Ice	1.309	Polystyrene	1.60
Water	1.33	Spinel, MgAl ₂ O ₃	1.72
Teflon	1.35	Sapphire, Al ₂ O ₃	1.76
Silica glass	1.458	Rutile, TiO ₂	2.68
Polymethyl methacrylate	1.49	Diamond	2.417
Silicate glass	1.50	Silicon	3.29
Polyethylene	1.52	Gallium arsenide	3.35
NaCl	1.54	Germanium	4.00

Snell's law of light refraction – refractive indices for light passing through from one medium with refractive index n through another of refractive index n' is related to the incident angle, θ , and refractive angle, θ' , by the following relation

$$\frac{n}{n'} = \frac{\sin \theta'}{\sin \theta}$$

If light passes from a medium with a high refractive index to one with a low refractive index, there is a critical angle of incidence, θ_c , which if increased will result in total internal reflection of the light. This angle is defined as θ' (refraction) = 90° .

Reflection: When a beam of photons strikes a material, some of the light is scattered at the interface between the two media even if both are transparent. Reflectivity, R , is a measure of fraction of incident light which is reflected at the interface, and is given by

$$R = \frac{I_R}{I_0}$$

Where I_0 and I_R are the incident and reflected beam intensities respectively. If the material is in a vacuum or in air:

$$R = \left(\frac{n-1}{n+1} \right)^2$$

If the material is in some other medium with an index of refraction of n_i , then:

$$R = \left(\frac{n-n_i}{n+n_i} \right)^2$$

The above equations apply to the reflection from a single surface and assume normal incidence. The value of R depends upon the angle of incidence. Materials with a high

index of refraction have a higher reflectivity than materials with a low index. Because the index of refraction varies with the wavelength of the photons, so does the reflectivity. In metals, the reflectivity is typically on the order of 0.90-0.95, whereas for glasses it is close to 0.05. The high reflectivity of metals is one reason that they are opaque. High reflectivity is desired in many applications including mirrors, coatings on glasses, etc.

Absorption: When a light beam is impinged on a material surface, portion of the incident beam that is not reflected by the material is either absorbed or transmitted through the material. The fraction of beam that is absorbed is related to the thickness of the materials and the manner in which the photons interact with the material's structure. Thus, according to *Bouguer's law*:

$$I = I_0 \exp(-\alpha \cdot x)$$

where I – intensity of the beam coming out of the material, I_0 – intensity of the incident beam, x – path through which the photons move, and α – linear absorption coefficient, which is characteristic of a particular material.

Absorption in materials occurs mainly by two mechanisms (1) Rayleigh scattering – where photon interacts with the electrons orbiting an atom and is deflected without any change in photon energy. This is significant for high atomic number atoms and low photon energies. Ex.: Blue color in the sunlight gets scattered more than other colors in the visible spectrum and thus making sky look blue. *Tyndall effect* is where scattering occurs from particles much larger than the wavelength of light. Ex.: Clouds look white. (2) Compton scattering – here incident photon knocks out an electron from the atom losing some of its energy during the process. This is also significant for high atomic number atoms and low photon energies. *Photoelectric effect* occurs when photon energy is consumed to release an electron from atom nucleus. This effect arises from the fact that the potential energy barrier for electrons is finite at the surface of the metal. Absorption occurs at particular levels of photon energies, which are equal to that of binding energies. The energy at which this occurs is called the absorption edge.

Transmission: the fraction of beam that is not reflected or absorbed is transmitted through the material. Thus the fraction of light that is transmitted through a transparent material depends on the losses incurred by absorption and reflection. Thus,

$$R + A + T = 1$$

where R – reflectivity, A – absorptivity, and T – transmittivity. Each of these parameters are characteristic of material, and they also depend on light wavelength.

If the incident light is of intensity I_0 , then the loss due to reflection at the front end of the material is RI_0 . Thus the fraction of beam intensity entering the material is

$$I_{\text{after reflection}} = (1 - R)I_0$$

Once the beam enters the material, a portion of it is absorbed. Thus

$$I_{\text{after absorption}} = (1 - R)I_0 \exp(-\alpha.x)$$

Before the beam exits at the back surface, a portion of it will be reflected again. Thus

$$I_{\text{after reflection at back surface}} = R(1 - R)I_0 \exp(-\alpha.x)$$

Thus, the fraction of beam that is actually transmitted through the material is given by

$$I_{\text{transmitted}} = I_{\text{after absorption}} - I_{\text{after reflection at back surface}} = (1 - R)I_0 \exp(-\alpha.x) - R(1 - R)I_0 \exp(-\alpha.x)$$

$$\text{Thus, } I_t = I_0(1 - R)^2 \exp(-\alpha.x)$$

The process of light transmission is shown schematically in the *figure 17.3*.

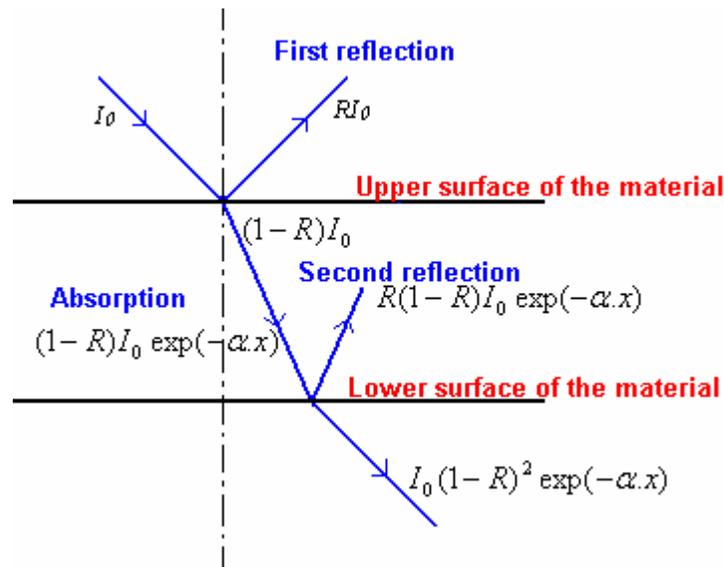


Figure-17.3: *Light transmission.*

17.4 Optical phenomena

As mentioned in earlier sections, light interacts with a material in many ways. Depending on the material, its crystal-/micro-structure, and also on the characteristics of incident light, there are many peculiar phenomena occurs, which are known as optical phenomena. These include: luminescence, lasers, thermal emission, photo-conductivity, and optical fibers. All these find quite many applications in technology for every day life.

Luminescence: Luminescence is defined as the process in which a material absorbs energy and then immediately emits visible or near-visible radiation. This occurs as a

result of excitation of electrons of a material from the valence band into the conduction band. The source of input energy may be high energy electrons *or* light photons. During luminescence, the excited electrons drop back to lower energy levels. If the emission takes place within 10^{-8} sec.s after excitation, the luminescence is called *fluorescence*, and if it takes longer than 10^{-8} sec.s, it is known as *phosphorescence*.

Luminescence takes place in outer valence- and conduction- bands, while x-rays are produced during electron transitions in the inner-energy levels of an atom. Luminescence does not occur in metals. In certain ceramics and semi-conductors, however, the energy gap between the valence and conduction bands is such that an electron dropping through this gap produces a photon in the visible range.

Ordinarily pure materials do not display this phenomenon. Special materials called *phosphors* have the capability of absorbing high-energy radiation and spontaneously emitting lower-energy radiation. Ex.: some sulfides, oxides, tungstates, and few organic materials. The emission spectra of these are controlled by added impurities referred as *activators* which provide discrete energy levels in the gap between valence and conduction bands. The excited electrons first drop to donor level, and get trapped. When the source is removed, they gradually escape the trap and emit light over some additional period of time. The intensity of the luminescence is given by

$$I = I_0 \exp\left(-\frac{t}{\tau}\right)$$

where I_0 – initial intensity of luminescence, I – fraction of luminescence after time, t , τ - relaxation time, constant for a material.

Luminescence process is classified based on the energy source for electron excitation as *photo-luminescence*, *cathode-luminescence*, and *electro-luminescence*.

Photo-luminescence occurs in fluorescent lamps. Here ultra-violet radiation from low-pressure mercury arc is converted to visible light by calcium halo-phosphate phosphor ($\text{Ca}_{10}\text{F}_2\text{P}_6\text{O}_{24}$). In commercial lamps, about 20% of F^- ions are replaced with Cl^- ions. Antimony, Sb^{3+} , ions provide a blue emission while manganese, Mn^{2+} , ions provide an orange-red emission band.

Cathode-luminescence is produced by an energized cathode which generates a beam of high-energy bombarding electrons. Applications of these include: electron microscope; cathode-ray oscilloscope; color television screens. Here, however, relaxation time must not be too long which makes the picture blur or they may even overlap. The modern televisions have very narrow, about 0.25 mm wide, vertical stripes of red-, green-, and blue- emitting phosphors deposited on the inner surface of the screens. With help of steel shadow mask with small elongated holes, the incoming signal is scanned over the entire screen at 30 times per second. The small and large number of phosphors consecutively exposed in the rapid scan of 15750 horizontal lines per second. The persistence of human eye makes possible a clear visible picture with good resolution. Commercial phosphors

for different colors are: red – yttrium oxy-sulfide (Y_2O_2S) with 3% europium (Eu); green – $(Zn,Cd)S$ with a Cu^+ acceptor and Al^{3+} donor; blue – zinc sulfide (ZnS) with Ag^+ acceptor and Cl^- donor.

Electro-luminescence occurs in devices with p-n rectifying junctions which are stimulated by an externally applied voltage. When a forward biased voltage is applied across the device, electrons and holes recombine at the junction and emit photons in the visible range (mono-chromatic light i.e. single color). These diodes are called *light emitting diodes* (LEDs). The characteristic color of an LED depends on the particular semi-conducting material that is used. GaAs, GaP, GaAlAs, and GaAsP are typical materials for LEDs. LEDs emit light of many colors, from red to violet, depending on the composition of the semiconductor material used. Some even emit light outside of the visible spectrum, i.e., infrared and ultraviolet. The following *table 17.2* lists materials used in different colored LEDs.

Table-17.2: *Materials for colored LEDs.*

Wave length (nm)	Color	Material
-	Infra-red	GaAs
660	Red	$GaP_{0.40}As_{0.60}$ or $Al_{0.25}Ga_{0.75}As$
635	Orange	$GaP_{0.65}As_{0.35}$
578	Yellow	$GaP_{0.85}As_{0.15}$
556	Green	GaP ($GaP_{1.00}As_{0.00}$)
-	Blue	$Ga_{0.94}NIn_{0.06}$

Lasers: Laser is an acronym for *light amplification by stimulated emission of radiation*. It is in fact special application of luminescence. Unlike most radiation processes, such as luminescence, which produce incoherent light, the light produced by laser emission is coherent i.e. light waves are all in phase with each other. Consequently, laser light waves are does not spread out i.e. parallel, directional, and monochromatic i.e. entirely of one wavelength.

In certain materials, electrons excited by a stimulus produce photons which in turn excite additional photons of identical wavelength. Thus a large amplification of the photons emitted in the material occurs. By selecting stimulant and material properly, laser beam can be in the visible range. Lasers are useful in many applications such as welding, metal cutting, heat treatment, surgery, mapping, reading compact disks, etc. A variety of materials are used to produce lasers. Ex.: Ruby, single crystal of Al_2O_3 doped with little amount of Cr_2O_3 ; yttrium aluminium garnet ($Y_3Al_5O_{12}$ – YAG) doped with neodymium, Nd; CO_2 gas; He-Ne gas; some semi-conductors like GaAs and InGaAsP. Gas lasers generally produce lower intensities and powers, but are more suitable for continuous operation since solid-state lasers generate appreciable amounts of heat.

Laser operation: when the laser material is exposed to stimulant, for example flash lamp, electrons that initially fills the lowest-energy levels gets excited into higher energy-levels. These electrons can decay back by two paths: one in which they fall directly back –

associated photon emissions are not part of the laser beam; others decay into a intermediate meta-stable state where they reside for about 3 ms before spontaneous emission. This initial spontaneous emission acts as stimulus and triggers an avalanche of emissions from remaining electrons in the meta-stable state. The photons are of the same energy and are in phase. The beam is collimated through the use of a tube with silvered mirrors at each end. As stimulated emission occurs, only those photons traveling nearly parallel to the log axis of the material are reflected. These reflected photons stimulate the emission of more photons. Reflected photons traveling up and down the length of the crystal produce ever-increasing number of stimulated photons. Finally, high-energy, highly-collimated, monochromatic beam of coherent light is emitted from the laser device.

Thermal emission: When a material is heated, electrons are excited to higher energy levels, particularly in the outer energy levels where the electrons are less strongly bound to the nucleus. These excited electrons, upon dropping back to the ground state, release photons in process what is called *thermal emission*.

During thermal emission a continuous spectrum of radiation is emitted with a minimum wavelength and the intensity distribution is dependent on the temperature. Higher the temperature, wider will be the range of wavelengths emitted. By measuring the intensity of a narrow band of the emitted wavelengths with a pyrometer, material's temperature can be estimated.

Photo-conductivity: As mentioned in earlier section upon absorption of photons at surface, electron may be released from its atom nucleus. Thus electricity can be generated from the surface of a metal when it is bombarded with photons. Similarly, bombardment of semiconductors by photons, with energy equal to greater than the band gap, may result in creation of electron-hole pairs that can be used to generate current. This process is called photo-conductivity, and is different from photo-electric effect in the sense that an electron-hole pair is generated whose energy is related to the band gap energy instead of free electron alone whose energy is related to the Fermi level. The current produced in photo-conductivity is directly related to the incident light intensity.

This phenomenon is utilized in photographic light meters. Cadmium sulfide (CdS) is commonly used for the detection of visible light, as in light meters. Photo-conductivity is also the underlying principle of the photo-voltaic cell, known to common man as solar cell, used for conversion of solar energy into electricity.

Optical fibers: Recently the buzz word in the communications sector is the optical fiber, using in place of metallic copper wires. Signal transmission through a metallic wire conductor is electronic, whereas in fibers it is photonic i.e. by photons. This enables faster transmission at higher densities to longer distances with reduction in error rate. These systems consists of transmitter (a semiconductor laser) to convert electrical signals to light signals, optical fiber to transmit the light signals, and a photodiode to convert light signals back to electrical signals.

Optical fiber is the heart of the communication system. It must have extremely low loss of light, must be able to guide the light pulses over long distances without significant loss and/or distortion. It primarily consists of core, cladding and coating. The core transmits the signals, while the cladding constrains the light beam to the core; outer coating protects the core and cladding from the external environment. Optical fiber operates on the principle of total internal reflectance. Typically both the core and cladding are made of special types of glass with carefully controlled indices of refraction. The indices of refraction are selected such that

$$n_{cladding} < n_{core}$$

Once the light enters the core from the source, it is reflected internally and propagates along the length of the fiber. Internal reflection is accomplished by varying the index of refraction of the core and cladding glass materials. Usually two designs are employed in this regard. In step-index optical fiber, there is a sharp change in refractive index between the core and cladding. In this design output pulse will be broader than the input one. It is because light rays traveling in different trajectories have a variety of path lengths. It is possible to avoid pulse broadening by using graded-index fiber. This results in a helical path for the light rays, as opposed to zig-zag path in a step-index fiber. Here impurities such as boron oxide (B_2O_3) or germanium dioxide (GeO_2) are added to the silica glass such that the index of refraction varied gradually in parabolic manner across the cross section. This enables light to travel faster while close to the periphery than at the center. This avoids pulse broadening i.e. light rays arrive at output at approximately same time. Both step- and graded- index fibers are termed as multi-mode fibers. Third type optical fiber is called single-mode fiber in which light travels largely parallel to the fiber axis with little distortion of the digital light pulse. These are used for long transmission lines.

Core and cladding materials are selected not only on the basis of their refractive indices, but also on basis of ease of manufacturability, light loss, mechanical strength properties and dispersion properties. However, density (ρ) and refractive index (n) are critical. These two parameters are related approximately as

$$n = \frac{\rho + 10.4}{8.6}$$

High-purity silica-based glasses are used as fiber material, with fiber diameter ranging from 5 to 100 μm . The fibers are carefully fabricated to be virtually free from flaws, as a result, are extremely strong and flexible. Uniformity of fiber cross-sectional dimensions and core roundness are critical; allowable tolerances of these parameters are within a micro-meter over 1 km of length.

References

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