THERMAL MANAGEMENT COATINGS

Electromagnetic radiation is classified in two major groups: 1) thermal (or heat) radiation and, 2) nonthermal radiation.

In solids, the molecules and atoms are vibrating continuously. In a gas, the molecules are really moving around, continuously bumping into each other. Whatever the amount of molecular motion occurring in matter, the speed is related to the temperature. The hotter the material, the faster its molecules are vibrating or moving.

Electromagnetic radiation is produced whenever electric charges accelerate – that is, when they change either the speed or direction of their movement. In a hot object, the molecules are continuously vibrating (if a solid) or bumping into each other (if a liquid or gas), sending each other off in different directions and at different speeds. Each of these collisions produces electromagnetic radiation at frequencies all across the electromagnetic spectrum. However, the amount of radiation emitted at each frequency (or frequency band) depends on the temperature of the material producing the radiation. The shorter the wavelenth (and higher the frequency), the more energy the radiation carries.

Thus, any matter that is heated above absolute zero generates electromagnetic energy. The intensity of the emission and the distribution of frequencies on the electromagnetic spectrum depend upon the temperature of the emitting matter. Matter that emits thermal electromagnetic radiation (a blackbody or a "grey" body) has the following three characteristics:

1) A blackbody with a temperature higher than absolute zero emits some energy at <u>all</u> wavelengths.
2) A blackbody at higher temperature emits more energy at <u>all</u> wavelengths than does a cooler one.
3) The higher the temperature, the shorter the wavelength at which the <u>maximum</u> energy is emitted.

The following diagram demonstrates these characteristics:

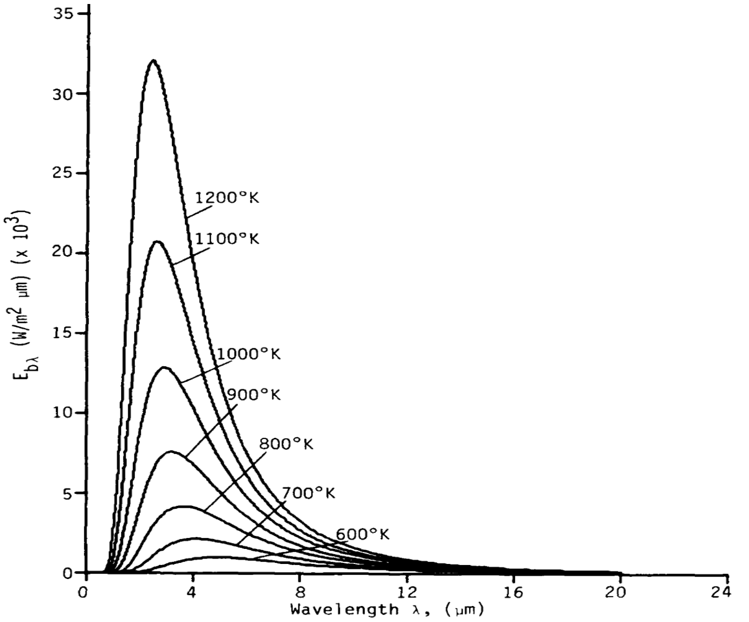


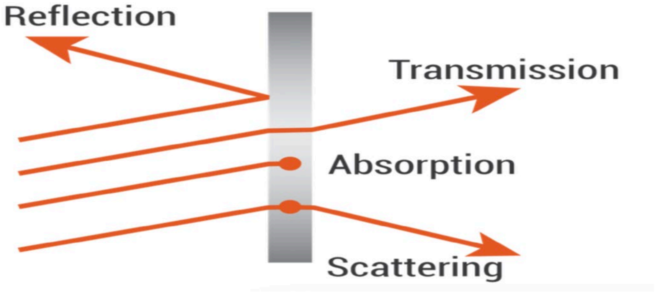
Figure 3 Monochromatic emissive power of a black body as a function of wavelength and temperature

As the temperature and resulting internal energy of a blackbody is increased, the peak wavelength of energy emitted over all wavelengths of the electromagnetic spectrum shifts to lower and lower value (higher and higher frequencies and energies), from infrared to visible to ultraviolet, etc. In addition, the "brightness" of the object (intensity and amount of energy) increases as the temperature increases. Thus, as the temperature is raised the amount of visible energy becomes greater and greater (it starts glowing red, then orange, then yellow, etc.).

This radiated heat energy is different from the energy emitted from objects that we perceive having different colors in the visible wavelengths – which is caused by electron transitions that our eyes perceive. During thermal radiation, thermal energy (heat) is converted via kinetic energy (vibration) into electromagnetic energy (light) and this energy is emitted at wavelengths encompasing the entire electromagnetic spectrum. During this process, the energy of the released photons and, consequently, the wavelength of the emitted light depends largely on the temperature of the heated light source, but it also depends on other characteristics of the object from which it is being emitted, such as spectral absorptivity and spectral emissive power. It is for this reason that the process of thermal radiation never produces a monochromatic light.

In contrast, nonthermal radiation is not caused by heat and occurs at lower temperatures and is therefore sometimes called 'cold light.' In this process, it is not the entire atom/molecule that accumulates and releases electromagnetic radiation, but solely one electron within the atom that is moved to a higher energy state, leading it to release some of its energy as electromagnetic radiation. This is a "nonthermal" process. Here, the light color strictly depends on the characteristics of the emitting material, as each particular electron will carry a specific energy to be released, resulting in a monochromatic light.

According to the second law of thermodynamics, the transmission of thermal energy (radiation) occurs via the transfer of heat from a material or region of higher temperature (the hotter object) to a material or region of lower temperature (the cooler object). When radiant energy reaches a surface of the cooler object, the energy can be absorbed, transmitted (through), or reflected (or any combination). The sum of these three effects equals the total energy transmitted, and the parameters that describe these three phenomena are given by $\alpha + \rho + \tau = 1$, where α represents spectral absorption factor, ρ represents the spectral reflection factor, and τ represents the spectral transmission factor.



The spectral absorption factor (α) is a function of the specific heat (C_p) of the material receiving the heat radiation. The specific heat of a material is defined as the heat required to raise the temperature of the material 1ºC. The amount of heat absorbed depends on whether the atoms/molecules in the material vibrate at the wavelength (frequency) of the incoming thermal radiation. When the material is one of high specific heat, it can absorb a large amount of heat before its temperature goes up. Since the second law of thermodynamics requires heat flow to occur from a hot body to a cold body, if the temperature of the hot body is kept relatively cold, the heat does not flow to a colder body very quickly since the difference in temperatures between the hot body and the cold body is relatively smaller than if the hot body were a material of low heat capacity.

Kirchoff's Law states that at thermal equilibrium, the power *radiated* by an object must be equal to the power *absorbed*." This leads to the observation that if an object absorbs 100 percent of the radiation incident upon it, it must reradiate 100 percent. This is the definition of a blackbody radiator.

However, most radiation sources are not blackbodies. Some of the energy incident upon them may be reflected or transmitted. The ratio of the radiant emittance W' of such a source and the radiant emittance W of a blackbody at the same temperature is called the emissivity (ε) of the source:

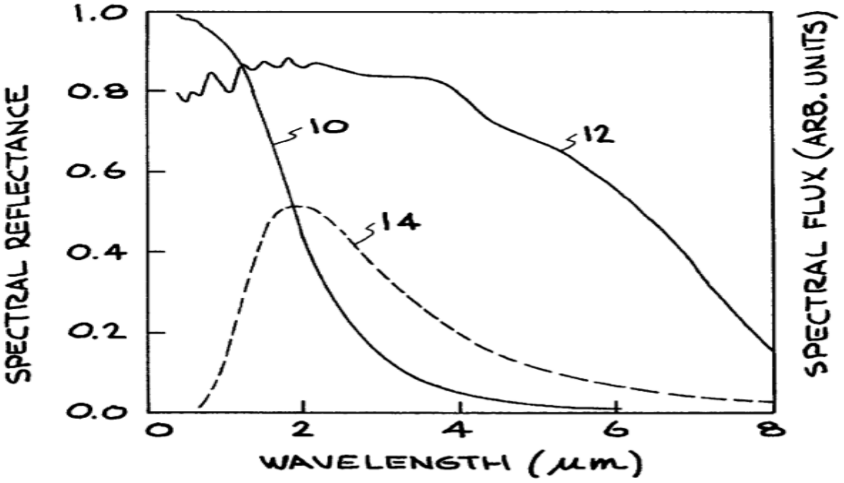
$$\varepsilon = W' / W$$

With this relation, different types of radiation sources can be classified. For a blackbody, ε = 1 over all wavelengths. The plot of this relationship is called Plank's curve. The curve for a graybody is proportional to Planck's curve for all wavelengths. The spectral radiant emittance for a selective radiator varies not only with temperature but also with wavelength. Materials with high absorption/emission are highly emissive materials, since most of the incident radiant energy is absorbed and not reflected. The material re-radiates the same frequency and amount of energy (minus reflections) as the incident absorbed energy. Thus the temperature of the emitted heat radiation is the same as the temperature of the absorbed heat radiation. Highly emissive materials are good materials for use in heat dissipating coatings, while highly reflective materials (below) are good materials for use in thermal barrier coatings. Emissive coatings are effective because, while they absorb heat from the hot side of a radiative body, that being the side at higher temperature (such as the inside of a pipe), they emit all of that heat to the cold side of the radiative body, that being the side at lower temperature (such as the outside of a pipe) [$T_{inside} - T_{inside} > 0$, so the driving force directs the heat from the inside of the pipe to the outside of the pipe].

Specular reflective materials (such as shiny metals) are good heat reflectors. Because the free valance electrons of these materials are not strongly attached to the atomic lattice, when hit by the incident photons, they do not transfer this energy to the lattice. That is, the incident energy is not absorbed by the lattice of the material. The skin effect is thus present, and the incident wave is “reflected”, and the metal does not absorb the incident energy.

This is why polished metals at low temperatures cannot efficiently absorb incident infrared energy.

For non-specular reflective materials, but rather materials that exhibit diffuse heat reflection (i.e. ceramic versus metallic materials), the spectral reflection factor (α) is a function of both the refractive index of the material receiving the heat radiation as well as the partical size when the particles are a pigment in a coating. Opaque, reflective surfaces such as those found on colored metal pigments such as aluminum and mica flakes also offer good reflectivity (U.S. Patent 6,468,647). The important physical data for inorganic pigments comprise not only optical constants, but also geometric data: mean particle size, particle size distribution, and particle shape. Particle size of the pigment is a very important parameter affecting heat reflectivity. Pigments containing the correct size particles significantly enhances the reflective properties. For the highest reflectivity, the particle size should be more than half the wavelength of the light to be reflected. Thus, for reflecting infrared light of 2μm wavelength (1,200 ºC peak wavelength) particle size should be >1-4μm.



Line 10 in the figure above shows the spectral reflectance as a function of wavelength for TiO_2 pigment particles of 0.22μm; Line 12 shows the spectral reflectance for TiO_2 pigment particles of 1.5μm; Line 14 shows the spectral distribution of 1,200ºC blackbody radiation. The figure clearly shows retention of reflectance throughout the 1-4μm wavelengths where blackbody radiation occurs at 1,200ºC.

The spectral transmission factor (τ) depends largely on the thermal conductivity (κ) of a material, which does not change with particle dimension. The effect of temperature on thermal conductivity is different for metals and nonmetals. In metals, heat conductivity is primarily due to free electrons. Following the Wiedemann–Franz law, thermal conductivity of metals is approximately proportional to the absolute temperature (K) times electrical conductivity. In pure metals the thermal conductivity decreases with increasing temperature and thus the product of the two, the thermal conductivity, stays approximately constant. In alloys the change in electrical conductivity is usually smaller and thus thermal conductivity increases with temperature, often proportionally to temperature.

On the other hand, heat conductivity in nonmetals is mainly due to grain boundary diffusion of heat in the material along the crystal lattice as well as lattice vibrations (phonons) in the crystal structure of the material itself. Except for high-quality crystals at low temperatures, the phonon mean free path is not reduced significantly at higher temperatures. Thus, the thermal conductivity of nonmetals is approximately constant at high temperatures.

Thermal diffusivity comes into play in thermal barrier coatings as a way to eliminate "hot spots" in the coating which might promote cracking through differential thermal expansion or contraction. Thus, coatings having high thermal diffusivity over coatings having low thermal diffusivity are preferred for thermal barrier coating applications.