Section 12.4

Paint

Many of our perceptions of the world come to us through our eyes. When we look at objects, we see that they are shiny or dull, bright or dark, colored or gray. However, what we're often seeing is actually paint. Paints are used everywhere to change the appearances of things—in architecture, art, consumer products, packaging, communications, food, and even on people. Paints also protect objects and modify their surfaces.

Questions To Think About: *How does paint dry? What is the difference between oil-based and latex house paint? What holds paints to surfaces? Why are some paints glossy while others are not? What is the difference between opaque and transparent paints? What determines paint's hiding power? Where does paint's color come from? Why are some paints red and others blue? What was lead doing in paint? What happens when you mix paints? Why does mixing red light and green light produce yellow light while mixing red paint and green paint produce brown-black paint?*

Experiments To Think About: *One of the most remarkable aspects of paint is that only a few primary colors are needed to create virtually any color of paint. Take a look at a color picture in a newspaper. The printing in newspapers is fairly coarse and you can see how a few primary colors are used to form the image. The picture consists of many tiny colored dots that come in only four colors: yellow, cyan, magenta, and black. These dots work together to create the impression of full color. A similar technique is used in color photographs. These pictures don't attempt to recreate the light exactly as it existed in the original scene. They simply make your eye experience the same patterns of stimulation as it would have in viewing the original scene.*

Formulating Paint

Paints are more than just colors we apply to surfaces. They are sophisticated coatings serving a variety of purposes. In addition to coloration, paints protect surfaces, change their shapes, and alter their physical properties. Let's begin by considering paints as coatings and turn later on to the issue of color.

Most paints include at least four groups of components: binders, volatile substances, pigments, and additives. Binders give paints their structures. They create the continuous coatings that stick to surfaces and remain in place indefinitely. In almost all cases, these coatings are polymers, the systems of giant string-like organic molecules that are discussed in Section 16.3. These molecules interlock with one another like noodles in a bowl of cold spaghetti to form rigid materials. Depending on the paint, these long molecules may already exist in the paint before application or they may form as the paint "dries."

Volatile substances are chemicals that keep the paints fluid enough to be applied easily and that subsequently evaporate during drying. In some cases, these volatile substances actually dissolve the binders and other chemicals so that the paint is nearly a uniform liquid. But other, more modern paints actually contain tiny solid binder particles that are suspended in the volatile substances. These particles become a continuous coating as the volatile substances evaporate.

Pigments are finely divided, insoluble powders that give a coating its color, opacity, and other optical properties. These powder particles are normally suspended in the paint when it's fluid and become trapped in the polymer molecules as the paint dries. There are some coatings that don't contain pigments, such as clear varnishes. There are also coatings in which the pigments do more than simply provide color, such as magnetic recording media. There are even pigments in which capsules break and release scents and essential oils when you scratch the paint.

Additives help these three components work together to form a uniform coating. Some additives aid in the drying process by initiating the formation of polymer molecules out of much smaller molecules. Others help keep the binder or pigment particles from clumping together before the paint is used or help prevent freezing. Still others alter paint’s viscosity to make it easy to apply.

CHECK YOUR UNDERSTANDING #1: Going For a Run

Sometimes a painter will add paint thinner to an oil-based paint or water to a latex paint. Why?

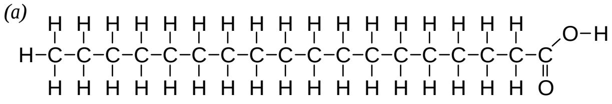
Artist's Oil Paints

Three interesting examples of paint are artist's oil paints, oil-based house paints, and latex house paints. Artist's oil paints are principally pigment particles suspended in *drying oil*. The drying oil forms the binder and consists of moderately large molecules that join together into long chains and tangled networks when exposed to oxygen for long periods of time.

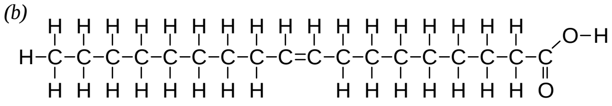
Like all natural oil molecules, a drying oil contains chains of carbon atoms. These carbon atoms attach to one another by sharing their outermost or valence electrons. Such covalent bonds normally involve only a single valence electron from each carbon atom and are called **single bonds**. Since a carbon atom has four valence electrons, it can form single bonds with four atoms.

Many oil molecules, particularly those in animal oils, contain chains of carbon atoms connected exclusively by single bonds (Fig. 12.4.1*a*). Each carbon atom that's not at the end of a chain is attached to two other carbon atoms and two hydrogen atoms. These oil molecules are *saturated* because they contain as many hydrogen atoms as the carbon atoms can hold. Saturated oils are liquid only at relatively warm temperatures, so they're most common in warm-blooded animals and tropical plants. Saturated oils don't harden in air and aren't drying oils.

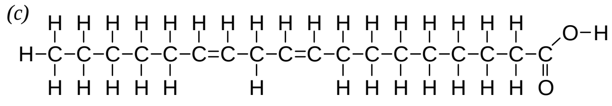
An unsaturated oil has at least one pair of carbon atoms that share two valence electrons from each atom. In that case, the carbon atoms are joined by a **double bond**. This double bond is slightly stronger than a single bond and it draws the two carbon atoms slightly closer together. But its most obvious effect is



Chain in animal oil (stearic acid)



Chain in monounsaturated vegetable oil (oleic acid)



Chain in polyunsaturated vegetable oil (linoleic acid)

Fig. 12.4.1 - Oils contain chains of carbon atoms (C) decorated with hydrogen atoms (H). (*a*) Saturated oils contain only single bonds between carbon atoms, while (*b*) monounsaturated oils have one double bond per chain. (*c*) Polyunsaturated oils have two or more double bonds per chain. These drawings are simplified because the chains aren't really straight or two-dimensional.

to decrease the number of hydrogen atoms in the molecule. With only two remaining valence electrons, each carbon atom involved in a double bond can only attach to two other atoms. Usually one is another carbon atom and the other is a hydrogen atom.

Since an oil molecule with double bonds has fewer hydrogen atoms than it would have if it had only single bonds, it's said to be *unsaturated*. An oil molecule that contains one double bond per chain of carbon atoms is *monounsaturated* while a molecule with more than one double bond per chain is *polyunsaturated*. Double bonds affect the shapes of oil molecules and make it more difficult from them to solidify. Unsaturated oils are liquid even at relatively low temperatures, so they're most common in plants from more temperate regions and in cold-blooded animals such as fish. In general, the colder a plant or cold-blooded animal's natural environment, the more double bonds are found in its oil molecules.

Double bonds are vulnerable to chemical attach and can link unsaturated oil molecules together. When a molecular fragment called a **free radical** attacks a double bond, the bond suddenly becomes a single bond. The free radical binds onto one of the carbon atoms and becomes its fourth partner. But the other carbon atom is left to seek a new fourth partner for itself. If it attaches to a carbon atom from another oil molecule, it permanently links the two oil molecules together. This cross-linking process, a form of *polymerization*, is what makes drying oils harden (Fig. 12.4.2).

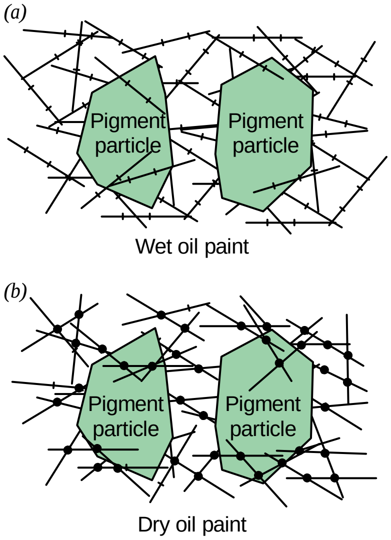


Fig. 12.4.2 - (*a*) In wet oil paint, the oil molecules (represented by lines with tick marks at the double bonds) move as a liquid around the pigment particles. (*b*) In dry oil paint, the oil molecules have become attached to one another at the sites of the former double bonds. These drawings are highly simplified since oil molecules are more complicated than they appear here.

Drying oils are polyunsaturated oils. Having several double bonds allows each chain to link with several other chains to form an intricate, interlocking network. The best drying oils have three or more double bonds per chain and these double bonds are well separated from one another. The classic drying oil is linseed oil, which has three evenly spaced double bonds in most of its chains. Linseed oil is obtained from flaxseed and was once a by-product of the linen-making process. Now that modern fabrics have replaced flax in linens, flax is grown primarily for the oil in its seeds.

The cross-linking process involves oxygen, which is essential to the formation of the free radicals. When a drying oil is exposed to air, it gradually hardens into a tough, clear, flexible plastic. This hardening converts chemical potential energy into thermal energy and the drying oil becomes warm. While not normally a problem, this warming can cause spontaneous combustion when paint-soaked rags are left to harden in a confined spaced.

While it normally takes weeks or months for pure drying oil to harden, adding various metal compounds to the paint can speed up the process. Certain metal atoms catalyze the formation of free radicals so that cross-linking occurs more frequently. Cobalt and manganese atoms help to harden the oil's surface while lead and zirconium help to harden the body of the oil. Because of lead's toxicity, it's no longer used as a drying agent.

Even with added drying agents, some time elapses before a drying oil begins to harden. Drying oils contain small amounts of antioxidants, which react with and eliminate free radicals. These antioxidants must be used up before the oil begins to harden. Similar antioxidants, such as vitamin E, slow such cross-linking processes in our own bodies and delay aging at a molecular level.

Artist's oil paints are made by mixing pigments with drying oils. The oils bind the pigment particles together and hold them onto the canvas. When first applied, the paint is a thick fluid that can be moved about easily. But the paint becomes thicker and thicker as the cross-linking progresses and it eventually solidifies completely.

CHECK YOUR UNDERSTANDING #2: Low in Polyunsaturated Fats

Why doesn't butter harden when it stands in air?

Oil-Based House Paints

Oil-based house paints are somewhat different from artist's paints. Most oil-based paints contain polymer binders dissolved in organic solvents. These polymer molecules are formed in the factory but float about separately in the liquid solvent (Fig. 12.4.3). Since no one wants water-soluble house paints, paint polymers are insoluble in water and require appropriate solvent chemicals. While only enough solvent is added to make the paint spreadable, solvents usual exceed 25% of the paint's weight. When you apply the paint to a surface, the solvent molecules evaporate into the air and the polymer molecules are left behind as a thin plastic layer. Most acrylic paints are of this type.

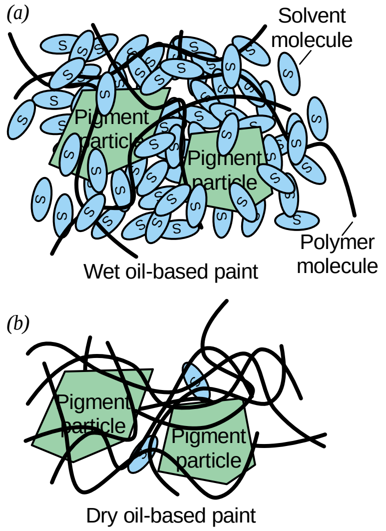


Fig. 12.4.3 - (*a*) Wet oil-based paint contains pigment particles suspended in a solvent containing independent polymer molecules. The solvent molecules evaporate as the paint dries. (*b*) Once the paint is dry, the pigment particles and a few solvent molecules are trapped in a tangled network of polymer molecules. The polymer molecules have some mobility only above the polymer's glass transition temperature.

For the polymer to dissolve in the solvent, its molecules must be attracted fairly strongly to those of the solvent. The polymer molecules must also be able to untangle from one another so that they can be carried away in the solvent. But while the polymer molecules of the binder dissolve completely in the solvent, the pigment particles in these paints do not. They remain solid and tend to settle to the bottom of the paint can as the paint sits on the shelf. That's why you must stir oil-based paints before you use them.

When you apply the paint, it must spread out on the surface rather than beading up into droplets (Fig. 12.4.4). The paint must **wet** the surface. Wetting occurs when the molecules in a liquid are attracted strongly enough to the surface molecules to bind to the surface molecules instead of one another. Not all liquids wet any particular surface. For example, water beads up on wax because water molecules aren't attracted strongly to wax molecules. Oil-based paints tend to wet most surfaces, although those surfaces should be clean and dry. Oil-based paints won't wet damp surfaces, just as water-based paints (the latex paints discussed below) won't wet oily surfaces. Sometimes primer coats are used to help the final paint wet and bond to the surface being painted.

Once you apply the paint, the solvent begins to evaporate from its surface. At first the solvent molecules travel easily through the open gaps between polymer molecules and the entire layer of paint dries together. Even the relatively large pigment particles drift freely about in the fluid. But as the solvent evaporates, the polymer molecules move closer together and the paint's viscosity increases. First the pigment particles stop moving, then the polymer molecules, and finally the solvent itself becomes immobile. At that point, the paint feels dry to the touch.

This drying sequence creates a thin layer of clear polymer at the very surface of the paint. As it evaporates, the solvent tends to carry polymer molecules past the larger pigment molecules to the surface of the paint. Even after the pigment molecules have become immobilized, the solvent and polymer still diffuse past them and create a micron-thick region of clear polymer at the surface.

This smooth, clear surface region is what gives many oil-based paints their glossy appearance. Most enamel paints achieve their high gloss by being oil-based. When light travels from air into the polymer layer, the light experiences an impedance mismatch and part of it reflects. Because the surface is smooth and flat, this reflection is *specular* (mirror-like) (Fig. 12.4.5). Light arriving at the surface from one direction reflects only in one direction.

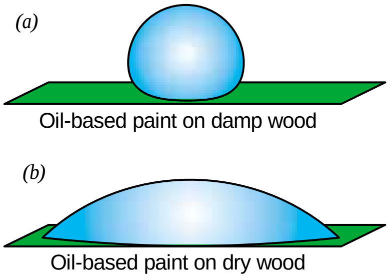


Fig. 12.4.4 - (*a*) Oil-based paints bead up on damp surfaces but (*b*) wet most surfaces that are dry and clean.

An irregular surface with features that are as large or larger than a wavelength of light scatters light irregularly and has a dull reflection. Sometimes oil-based paints are made "semi-gloss" or even "flat" by including very fine particles of silicon dioxide (quartz sand) in the mixture. These quartz particles are smaller than pigment particles and diffuse to the surface of the paint as it dries. They spoil the smoothness of the surface and weaken or eliminate the specular reflection. Similarly, when pigment particles begin to protrude through the polymer surface of weathered or worn paint, the appearance is flat.

Most oil-based paints never dry completely without baking. Although the solvent molecules diffuse rapidly to the surface and evaporate early on, they have more and more trouble leaving as the paint becomes more viscous. Eventually, the polymer tangle becomes so dense that even the tiny solvent molecules can't work their way through it. What appears to be dry paint actually contains a substantial amount of trapped solvent. The occasional solvent molecules that do escape give the paint its long-lasting odor.

The polymer tangle is a type of glass (a non-crystalline solid discussed in Section 17.2). To eliminate solvent molecules trapped in the glassy polymer, it must be warmed until its molecules begin to move past one another. Exceeding this **glass transition temperature** brings a degree of mobility to the molecules and allows the trapped solvent to escape. Paints and coatings that come into contact with foods are always baked after application to drive out the solvents.

Because of their rigid, impermeable natures, oil-based exterior house paints tend to bubble and crack. Water migrates through wood and gets under the layer of paint. This water is unable to escape through the paint and can create blisters when the paint is heated by sunlight. Changes in temperature and moisture content also cause the wood to expand and contract. Rigid oil-based paint experiences different relative expansions and contractions and it can buckle or crack.

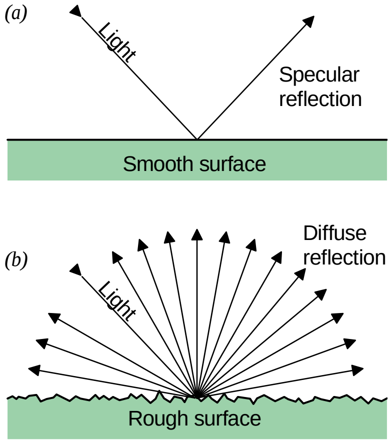


Fig. 12.4.5 - (*a*) Surfaces that are smooth on the scale of a wavelength of light create a mirror-like or specular reflection. (*b*) Surfaces that are rough give a diffuse reflection and appear dull or "flat."

But inside, oil-based paints are very durable. Their hardness and rigidity make them easy to clean. Dirt sits on the surface of these paints and can be removed with anything that doesn't damage the polymer itself. Professional painters, who don't mind cleaning their brushes and equipment with solvents, generally prefer oil-based interior paints. Do-it-yourselfers usually find it easier to use the latex paints discussed below.

Many oil-based house paints exhibit drying oil behavior, too. As the solvent evaporates and oxygen enters the paint, cross-linking occurs between the polymer chains. Most alkyd paints are of this type. The cross-linking process creates many tiny fragment molecules that evaporate as the paint dries and give the paint its characteristic odor.

These drying oil-like paints use drying agents to speed up the cross-linking between double bonds. Unfortunately, the drying agents of choice until the 1930's were lead compounds. Since these paints are too rigid and impermeable to tolerate changes in temperature and moisture content, they eventually flake off woodwork and present a terrible health hazard, particularly for young children. Modern drying oil-like paints use relatively non-toxic drying agents.

However, lead-free oil-based paints still present a health risk: solvent content. The volatile organic solvents they contain are toxic. Given that oil-based paints require complete solution of water-insoluble polymers, there seems to be no way of eliminating organic solvents from them. What is happening is that painters and coaters are gradually abandoning oil-based paints and coatings in favor of those that don't involve complete solution of the polymers. The most important paints that don't involve complete solution are latex paints.

CHECK YOUR UNDERSTANDING #3: It’s Not Soluble Anymore

Some oil paints clean up with solvent while others are impossible to clean that way. What is the difference?

Latex House Paints

Latex house paints aren't uniform liquids. Like oil-based paints, latex paints contain polymer molecules but these molecules aren't dissolved in a solvent. Instead, they are incorporated in tiny solid particles that float around in a liquid carrier (Fig. 12.4.6*a*). The polymer molecules are actually insoluble in that carrier, which is usually water.

It may seem that such polymer particles could never get together to form a uniform coating, but they actually do. Once the paint is applied to a surface, the water evaporates and the polymer particles move closer together. They're pulled together by water as it leaves and their polymer chains begin to mingle together. By the time the water is gone, the molecules are tightly interwoven. They trap the paint's pigment particles and create a layer that's often more durable than that of an oil-based paint.

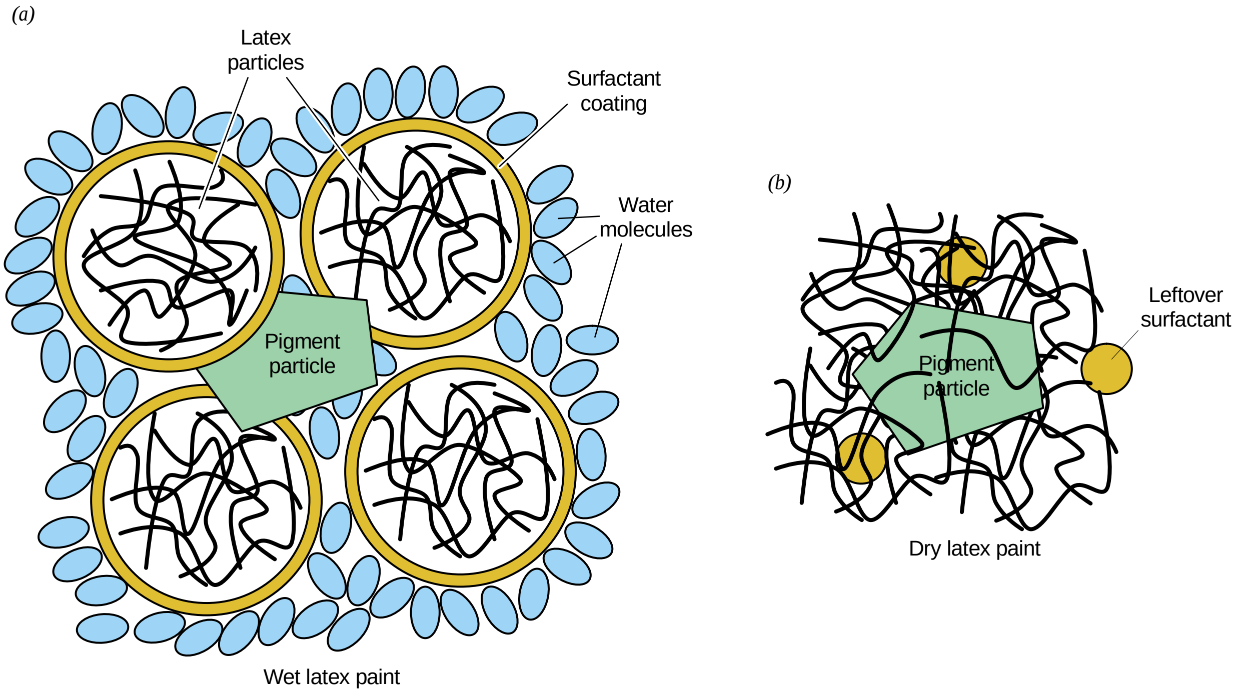
Latexes aren't simple to make. The polymer particles must remain suspended in the paint while it sits in the can and must not clump together before the paint begins to dry. Once the paint starts drying, the polymer particles should clump together. Obviously, this is a tricky business.

To keep the polymer particles suspended as an **emulsion**—one phase of material suspended as tiny particles in another phase of material—the particles are coated with special chemicals called **surfactants**. Surfactants are molecules such as soaps and detergents that naturally migrate to the interfaces between oils and water, and stabilize those interfaces (see Section 17.2 on Laundry). Surfactant molecules allow water to cling to the oil-like polymer particles. Each particle thus maintains at least a thin layer of water molecules around it, so that the polymer particles don't clump together while the paint is in the can.

But as water evaporates from drying latex paint, the remaining water pulls the polymer particles toward one another. The water molecules bind to one another and to the surfactant molecules with hydrogen bonds. The surfactant molecules cling to the polymer particles with van der Waals forces (see Section 17.1 on Oil Refineries). As water molecules leave the gaps between polymer particles, the remaining water molecules draw the polymer particles together. Eventually the polymer particles begin to touch and their polymer molecules become tangled together. The particles coalesce into a single material (Fig. 12.4.6*b*).

For the particles to coalesce properly, the polymer molecules must be able to move under the influence of thermal energy. Since this mobility vanishes be-

Fig. 12.4.6 - (*a*) Wet latex paint contains tiny spheres of polymer, coated with a surfactant, and suspended as an emulsion in water. (*b*) As the paint dries, the remaining water molecules pull the latex spheres together until they coalesce into a continuous film.



low the polymer's glass transition temperature, that glass transition temperature must be very low. But a low glass transition temperature is undesirable in the long run because the paint would remain sticky. Instead, the manufacturer usually adds a solvent that enters the polymer particles and reduces their glass transition temperatures temporarily. That way, the particles can touch and coalesce only until the solvent evaporates. Once the solvent is gone, the glass transition temperature increases and the paint loses its stickiness. In latex house paint, this final drying process takes a few weeks.

But on a hot summer day, the sun can warm dry latex paint above its glass transition temperature. The paint's polymer molecules then begin to move around and the paint readjusts to its situation. This readjustment is a good thing because it allows the paint to relieve tension and avoid cracking or blistering. Water vapor can escape between the polymer chains and the paint "breathes." That's why latex exterior paints are more durable than oil-based exterior paints.

Unfortunately, this movement of the polymer chains allows latex paint to pick up dirt. Dirt particles that land on the paint's surface in hot weather can become caught in the polymer chains, spoiling the appearance of the paint. Also, the paint tends to stick to itself in hot weather, a behavior called *blocking*. While blocking is useful for polymer-based adhesives like contact cement, it's terrible for paint. If you touch two freshly painted latex surfaces together, even if they feel dry, they will often block together. All in all, it's best to leave latex paint alone after painting until all of the solvent has evaporated from its polymer particles and its glass transition temperature has become as high as possible.

Because latex particles are large, they don't diffuse to the surface of the paint as the water evaporates. As a result, latex paint doesn't form a clear, pigment-free layer at its surface. The presence of pigment particles all the way to its surface makes latex paint rough on the scale of a wavelength of light. That's why latex paints aren't as glossy as oil-based paints.

Because the principal liquid in latex paints is water, latex paints contain less volatile organic chemicals than oil-based paints. However, most latex paints contain some organic solvent to soften the polymer particles so that they can coalesce easily. Most also contain organic solvents that slow down drying. If the only liquid in latex paint were water, it would dry so quickly that you couldn't work with it. Each brush stroke would harden by the time you returned with the next stroke and you would have trouble blending the strokes into a smooth layer. To slow down the drying, most latex paints include large quantities of ethylene and propylene glycols. These two volatile organic chemicals are the main ingredients in automobile antifreezes. They resemble water as solvents but they evaporate much more slowly. They also protect the can of paint from freezing, an event that would squeeze the latex particles together and ruin the paint.

Paints also contain other environmentally questionable chemicals. Fungi and bacteria will attack almost anything and paint is no exception. To prevent such attacks, paints include fungicides and bactericides. One common and extremely effective fungicide and bactericide is phenylmercuriacetate, an organic mercury compound. Because mercury is toxic, it was banned from interior use in 1990. However, it's still used in exterior paints.

CHECK YOUR UNDERSTANDING #4: If It's Not Too Late

Dried latex paint isn't affected by water so how can water clean it up before it dries?

White and Metallic Pigments

Pigment particles give paint its opacity, color, or both. Since these two characteristics, opacity and color, are somewhat independent of one another, we'll examine them separately.

Even pure white paint has pigment in it but this pigment absorbs no light. Instead, its particles scatter light almost perfectly in random directions. White pigment particles are clear but have very high refractive indices. When these particles are embedded in a polymer layer, they produce countless impedance mismatches in that layer. As light tries to pass through the paint, part of it reflects at every boundary between polymer and pigment, and almost none of the light reaches the back of the layer. Because the pigment particles are rough and randomly oriented, they scatter the light everywhere and it leaves the paint's surface as a diffuse glow. The paint appears white.

The best white pigments are those that have the highest refractive indices and the least tendency to absorb visible light. The higher the refractive index, the more severe the impedance mismatches and the more light is reflected at each boundary between polymer and pigment. This high reflectivity gives paint its *hiding power*—its ability to prevent light from reaching the material beneath the paint and then returning to paint's surface. Paints with very high refractive index pigments are best at hiding the surfaces they cover.

Perfect clarity in these pigments is important because any absorption of light will give the paint a color. For example, granules of salt and sugar are almost perfectly clear, which is why they appear white as light reflects from them. But adding light-absorbing food dyes to sugar causes it to appear colored.

Tiny particles of calcium compounds (lime, chalk, and gypsum) were used to whiten walls for millennia. However, these compounds have refractive indices of between 1.5 and 1.7, so their hiding power is poor. Until the 1930's, the most common white pigment in paint was white lead (lead carbonate). This clear compound has a refractive index of 1.94, so its hiding power is modest but better than that of the calcium compounds. However, white lead is quite toxic and is a nightmare for people living in pre-1930's buildings. Fortunately, white pigments with much better hiding powers have replaced it.

The most common white pigment in modern paints is titanium dioxide. This compound comes in two crystalline forms, rutile and anatase, each of which has a very high refractive index and near-perfect clarity. Rutile's refractive index is 2.76 while anatase's is 2.55. Its higher refractive index means that rutile particles are somewhat more reflective in paint than anatase particles. Because of its better reflectivity, rutile pigment has more hiding power than anatase pigment. However, rutile absorbs blue light slightly so that rutile-based white paint would have a yellow tint. For colored or off-white paints, rutile's slight coloration doesn't matter. However, pure white paints must use anatase.

Some paints use metal particles as pigments. These metallic pigments have enormous hiding powers because essentially zero light gets through a metal particle. But metals absorb a few percent of the light that hits them, converting light energy into thermal energy. Light entering a pile of round metal particles gets trapped bouncing between particles and is absorbed before it can work its way back out. Thus a pile of round metal particles appears black.

In contrast, metal flakes appear bright because they reflect light back out of the surface in a single reflection. Each flake acts as a tiny mirror and creates its own specular reflection. When metal flakes are incorporated in paint, they tend to lie roughly parallel to the surface and give the paint a shiny, metallic look. They don't create a single, mirror reflection because they're not perfectly aligned with one another. But they also don't scatter light uniformly in all directions like white pigment. Most metallic paints contain aluminum flakes or powders, although they may be colored to give the appearances of other metals.

Pearlescent and iridescent paints contain flakes of transparent materials that have been specially coated to enhance their reflectivities. These flakes produce specular reflections that may be colored by interferences between reflections from different surfaces. Because they transmit some of the light that strikes them, these flakes don't look metallic. They also lie roughly parallel to the surface in paint and give it an interesting appearance. Iridescent flakes are very popular in metallic car paints, giving them subtle colored highlights.

CHECK YOUR UNDERSTANDING #5: White as a Cloud

Why does a mist of water droplets appear white?

How We See Light and Color

Colored pigments give paints their colors by selectively absorbing some of the light striking the paint. Since the light reflected from the paint has a different spectrum of wavelengths than the light striking it, the reflected light looks colored. But to understand why it has a particular color, you must understand how we see light.

As noted in Section 15.1, high-frequency, short-wavelength visible light appears blue or violet to your eyes while low-frequency, long-wavelength visible light appears orange or red. But these relationships only apply to pure light—light having a single frequency and wavelength. As soon as you start to mix together lights of several different wavelengths, everything gets more complicated.

Your eyes don't make precise measurements of wavelength. Instead, your eyes look for three different ranges of wavelengths. Within the *retina* of your eye, there are specialized cells that only detect light of certain wavelengths. Some of these cells detect reddish light, others detect greenish light, and still others detect bluish light.

These three types of color sensitive cells are called *cone cells*. Cone cells are most abundant in the *fovea*—the region of high visual acuity near the center of the retina. You also have retinal cells that are more light-sensitive than cone cells but that can't distinguish color. These *rod cells* sense light and dark and provide you with night vision. Rod cells are most abundant in your peripheral vision. In the day, you see mostly with your color sensitive foveas. At night, you see mostly with your light-sensitive peripheral vision.

It might seem as through these three types of color sensors will only allow you to see three colors. But you know that you see a wide variety of colors. This variety of perceived colors comes about when two or more of the color sensors are stimulated at once (Fig. 12.4.7). Each sensor informs your brain about how much light it sees and your brain interprets the mixture of responses as a particular color.

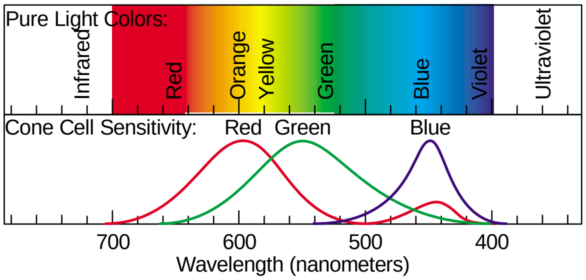


Fig. 12.4.7 - The red sensor cone cells detect light between about 400 and 700 nm, but are most sensitive to light near 600 nm. The green sensors are most sensitive around 550 nm and the blue sensors around 460 nm. The response of the red cone cells to short wavelength light allows you to perceive violet light.

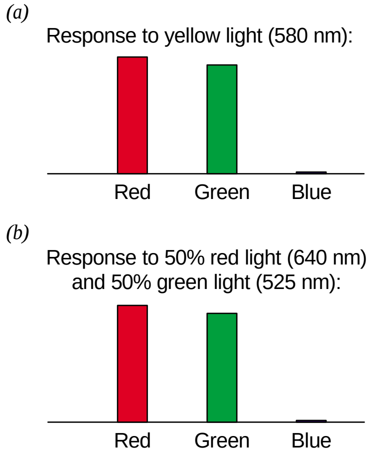


Fig. 12.4.8 - (*a*) When pure yellow light at 580 nm reaches your retina, the red and green sensor cells respond almost equally and you perceive yellow. (*b*) When an even mixture of pure red light at 640 nm and pure green light at 525 nm reaches your retina, the sensor cells respond in the same manner and you again perceive yellow.

In general, visible light of a particular wavelength stimulates all three types of cone cells to some extent. However, the cells don't respond equally to each wavelength of light. When you look at 680 nm (680 nanometer) light, the cone cells specialized for reddish light respond much more strongly than those specialized for greenish or bluish light. Because of this strong response by the red sensors, you perceive the light as being red.

But other wavelengths of light may stimulate the three types of cells somewhat more evenly. Yellow light at 580 nm is in between red and green light. Both the red sensitive cone cells and the green sensitive cone cells respond moderately when yellow light strikes them (Fig. 12.4.8*a*). Your brain understands from this balanced response that yellow light is present.

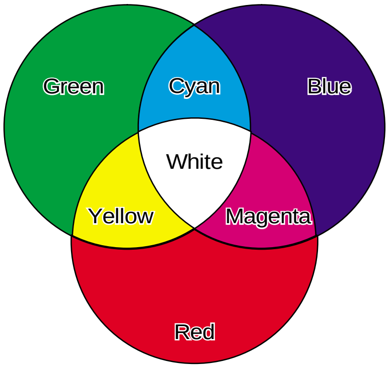
But the same response can be invoked from your retina by exposing it to an equal mixture of pure red and green lights (Fig. 12.4.8*b*). Again, both the red sensitive and green sensitive cone cells respond moderately and you see yellow. Even though there is no pure yellow light at 580 nm reaching your retina, you think that there is. You simply can't tell the two situations apart.

Thus your eyes are very easy to trick into seeing various colors. A mixture of pure red, green, and blue lights can make you see virtually any color. The only problem comes in choosing the pure red, green, and blue wavelengths. There aren't really any wavelengths that stimulate only the green sensor cells and the wavelengths that only stimulate the red or blue sensors are right at the edges of visibility, where you can hardly detect the light at all. Still, this is the technique used by a television. It creates relatively pure red, green, and blue lights with its phosphor dots and tricks your eyes into seeing any color it likes.

The technique of mixing red, green, and blue lights to produce colors is called **color addition**. Fig. 12.4.9 shows the effects of adding these three **primary colors of light** in equal amounts. By varying the amount of each primary color in the mixture, any color of light can be produced.

CHECK YOUR UNDERSTANDING #6: Mixing Colors

If you look at a mixture of 70% pure red light and 30% pure green light, what color will you see?



Additive colors

Fig. 12.4.9 - The three primary colors of light are red, green, and blue. These three colors can be mixed to make us see any possible color. Here green and red mix evenly to make yellow light; blue and red mix evenly to make magenta light; and green and blue mix evenly to make cyan light. When all three primary colors of light mix evenly, they produce white light.

Colored Pigments and Paint

But what about paint? It doesn't emit its own light; it only reflects light that you send at it. If you expose a paint to white light, how does it make you see colors?

The answer is that it selectively absorbs light until the remaining light has the right wavelengths to make you see the desired color. When you send white light at red paint, this paint absorbs light that would stimulate the green or blue sensors of your eyes. All that is left is light that stimulates your red sensors, so you see the paint as red. Green paint absorbs all but light that stimulates your green sensors and blue paint absorbs all but light that stimulates your blue sensors. You see this reflected light because the paint also contains white pigment, such as titanium dioxide, that reflects any unabsorbed light back from the paint.

Thus paints and colored pigments work by removing unwanted colors from the light they reflect. By carefully adjusting which wavelengths of light are absorbed and the extent of that absorption, you can create paint with any color you like. Most paint pigments are based on specific molecules that absorb light in a particular range of wavelengths. Many metal compounds, including those of copper, chromium, iron, antimony, nickel, and lead absorb certain wavelengths of light and appear brightly colored. Lead and lead-chromium compounds are particularly beautiful pigments for paints, but they are just too toxic to use. Organic pigments are also extremely effective and have replaced metal compounds in many paints. (For history of organic pigments, see ❐.)

Of course, many colors of paint are created by mixing different pigments together in carefully controlled amounts. What are the rules governing this mixing of pigments? The rules are those of **color subtraction**. If you start with white light and remove various amounts of the three primary colors of light, you can create any color of paint you like. If you remove all light, you arrive at black.

Since the goal of color subtraction is to remove the three primary colors of light in a controlled manner, the **primary colors of paint** are those pigments that remove only a single primary color of light from white light. These primary colors of paint are yellow (which absorbs blue light), cyan (which absorbs red light), and magenta (which absorbs green light). You may have learned the three primary colors of paint as yellow, blue, and red, but that group of pigments is not as flexible as yellow, cyan, and magenta. You really can make any color you like by mixing yellow, cyan, and magenta pigments.

For example, you can create green paint by mixing equal amounts of yellow and cyan pigments. The yellow pigment absorbs some blue light and the cyan pigment absorbs some red light. What is left is mostly green light. The more of each primary pigment you add to the paint, the more completely it will absorb its color of light and the deeper the color of the paint. Fig. 12.4.10 shows the effects of adding these three primary colors of paint in equal amounts so that each pigment completely absorbs its primary color of light. By varying the amount of each primary color in the mixture, any color of paint can be produced.

This technique of mixing primary colors of paint to produce any color is particular useful for printing photographs in newspapers, magazines, and books. It allows full color images to be created with only three colored inks, although most printers also use black ink to provide good contrast without having to use enormous amounts of colored pigment.

Inks are similar to paints except that they contain dissolved **dyes** rather than solid pigment particles and they don't contain any reflective white pigments. Inks themselves tend to be transparent but colored, and they rely on the underlying paper to reflect light. Paper consists mainly of cellulose, a clear natural polymer. Because this cellulose is finely divided in paper, it reflects light at each surface and the paper appears white. Often white paint pigments are applied to paper during manufacture to make the paper even whiter.

By varying the amounts of the four inks applied to each location on a printed page, the printer has complete control over the colors that you see when you look at it in white light. However, since each ink is applied separately to the page, the printer must be careful to overlap the inks perfectly. Careless color printing, such as often occurs in newspapers, creates blurry images when the yellow, cyan, magenta, and black ink images are shifted relative to one another.

In contrast, very high quality, high cost printing jobs are often done with more than four inks. Because the registration between the separate inks is never quite perfect, these fancy printing tasks are done with extra colors so that they can avoid having to mix colors directly on the page. Instead of trying to create a red letter "H" by first printing a yellow "H" and then a magenta "H" directly on top of it, the printer will actually use a red ink to print the "H" in a single step. The same printer may apply a clear varnish layer over every picture to give them a glossy appearance. This glossy look comes from the specular reflection at the surface, caused by the impedance mismatch between the air and the smooth layer of varnish.

Unfortunately, the light that pigment molecules absorb often damages the molecules. Blue and ultraviolet light, which carry large amounts of energy in each light packet—each photon—are particularly damaging. Thus molecules that absorb blue light, such as those creating red or green colors, tend to be destroyed

❐ As an 18-year-old student, **English chemist William Henry Perkin (1838–1907)** set about trying to synthesize the drug quinine. His technique was based on the simplistic understanding of organic chemistry at the time and couldn't possibly have worked. Instead, he discovered a dye he called aniline purple or mauve. Before his discovery, purple dyes were rare and costly. Purple clothing, once reserved for royalty, suddenly became available to the common person. Perkin established a company in Germany to manufacture this dye and thus founded the German dye industry.

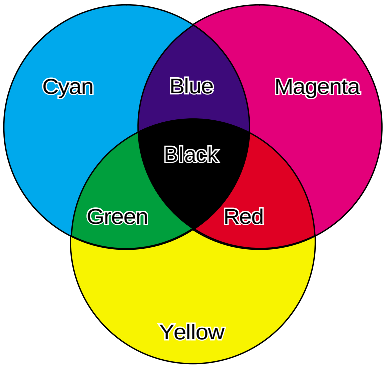


Fig. 12.4.10 - The three primary colors of paint are yellow, cyan, and magenta. These three colors can be mixed to make us see any possible color. Here cyan and yellow mix evenly to create green paint; cyan and magenta mix evenly to create blue paint; and yellow and magenta mix evenly to create red paint. When all three primary colors of paint mix evenly, they produce black paint.

by long exposure to sunlight. You have probably seen pictures or photographs that have been bleached by the sun. The red color pigments are destroyed first and the pictures appear bluish.

Protecting paints and surfaces from light damage is actually very important. Sunlight can damage not only the pigment molecules, but also the binder that holds the paint together. Often the white or metallic pigments in paint protect it and the surface beneath from light damage by absorbing or reflecting ultraviolet light. Titanium dioxide is particularly good at absorbing ultraviolet light. Sunscreens perform a similar protective role, absorbing ultraviolet light and preventing most of it from damaging your skin.

However, many of the pigments and binders used in artwork are simply too fragile to tolerate long exposure to blue or ultraviolet light. These paintings are often kept in low light conditions or viewed only with long-wavelength, yellowish light. While yellow light is less damaging to the molecules than white light, it affects the appearance of the paints. Paint can't reflect light that isn't there. While blue paint is supposed to reflect blue light, it looks black when there is no blue light to be reflected. The blue paint absorbs the red and green lights in the yellow illumination and there is just nothing else left. Clearly the viewing light affects the perceived colors of paint.

This viewing illumination problem creates problems for color matching. Two paints may look like a perfect match in one type of illumination but may appear significantly different in another illumination. For example, under red illumination blue and black paint both appear black but under white illumination they look different. Similarly, two paints that look identical in incandescent lighting will look somewhat different in fluorescent lighting. This behavior is called *metamerism* and can only be avoided by using exactly the same pigments in the two paints being matched. If you can't match the paints chemically, you must do the color matching in the proper lighting. However, metamerism is occasionally helpful, such as in reading faded old letters. In the proper illumination, the contrast between the ink and the paper may be greatly enhanced.

CHECK YOUR UNDERSTANDING #7: Getting the Red Out

Games and contests often hide secret messages in a highly colored picture. When you look at the picture through red plastic, you can read the message. How do these messages work?

Fluorescent Pigments

In most cases, pigments selectively absorb certain wavelengths of light and convert the energy in that light into thermal energy. However, there is one important exception to this rule: fluorescent pigments. These pigments turn only part of the light energy into thermal energy and reemit the rest as a new color of light. This absorption and reemission process is **fluorescence**, a topic discussed in Section 12.2. The new light is always longer in wavelength than the light that the pigment absorbed. For example, a red fluorescent pigment might absorb blue light and emit red light as a result. If you expose the red fluorescent pigment to blue light, it will glow red.

Fluorescent pigments and dyes are very popular in everything from clothes to marking pens. A fluorescent green shirt emits more green light than a white shirt does because the fluorescent green shirt actually converts the blue light that hits it into green light. Many white clothes or business cards appear to be whiter than white because they contain a fluorescent pigment or dye that converts ultraviolet light into white or blue-white light. They really do emit more visible light than a perfectly white, but non-fluorescent surface. Many laundry detergents include "brighteners" that are really fluorescent chemicals that cling to the clothes and turn ultraviolet light into visible light.

CHECK YOUR UNDERSTANDING #8: It Isn’t So Black After All

Fluorescent colors on clothes glow brightly in black (ultraviolet) light. Why?