

The Physics, Chemistry and Perception of Colored Flames

Part I

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SUMMARY

The first part of this three-part monograph presents an in-depth examination of the development of light theory; mechanisms of light generation in flames; atomic line, molecular band and continuous spectra; the definition, laws and measurement of color; chromaticity diagrams and how the pyrotechnist can use this knowledge of physics in planning colored flame formulations of optimal purity.

1.0 Preface

In my examination of pyrotechnic literature, I have not been able to find a comprehensive discussion of the physics, chemistry and perception of colored flames, let alone one that could be understood by the average fireworks enthusiast. The standard texts such as Davis (1943), Weingart (1947), Ellern (1968) and Lancaster (1972) treat the subject of color at the most cursory level. Technical reports prepared for the military usually deal with a very narrow aspect of the subject and the reader often must have an advanced knowledge of chemistry to understand them. In none of the pyrotechnic literature is the psychology and physiology of color perception considered. In light of some aspects of E. Land's recent theory of color perception, Land (1974), this may be a most serious omission. In writing this three part monograph, I hope to supply the general pyrotechnic community with a comprehensive discussion of the physics, chemistry and perception of colored flames.

I have attempted to write at a level such that most interested people will be able to follow the discussion, at least at a general level, and many will be able to understand the material in some detail. That is to say, quantum electrodynamics, nonequilibrium thermodynamics and molecular biology have been kept to an absolute minimum, if not eliminated altogether. I have often substitut-

ed analogy, semi-classical explanations, and a little hand waving in place of perfectly rigorous science. In doing this, I have been careful not to distort the science being discussed, but only to make the subject more understandable. I have included numerous drawings, notes and equations as figures. I hope the result is complete, accurate, useful, understandable, and may possibly even makes enjoyable reading.

2.0 Introduction

Many of the concepts discussed in this paper are not particularly easy to understand or to work with. It is reasonable to wonder why you should bother to read it and what you will get out of it. The answer is slightly different depending on your scientific background and on what type of pyrotechnist you are. I will assume your scientific background is limited. If you are the cookbook type, and enjoy trying formulations developed by others, you may expect to gain a better understanding of the art you are practicing. I suspect this better understanding will be satisfying and self-rewarding, but will not bear much tangible fruit. If you are an experimenter, developing your own color formulations, a fuller understanding of the physical principles involved should allow you to move faster toward successful conclusions in your development efforts. For example, you will know why and how chlorine donors are important in achieving good strontium reds, but are detrimental to lithium reds. Thus, if you were attempting to develop a good lithium carbonate red, you probably would not waste much time trying to find the best chlorine donor or how to use.

The material presented in this paper is organized along the lines suggested in the title. The first part discusses the physics of colored flame production, including the nature of light, the processes through which light is generated, and the definition and measurement of color. This material is more important than it may at first appear.

While it is relatively easy to interest pyrotechnists in the chemistry of colored flame production, chemistry is just the mechanism we use to accomplish the physics of colored light production. Without understanding physically what colored light is, how it originates, and the classical laws of additive color mixing, a discussion of chemistry would be of very limited value. For example, a discussion of the chemistry of ionization buffering would not be very useful or very interesting, unless you understood the physical reason why it can be important in generating intensely colored flames.

The second part of this paper discusses the chemistry of colored flame production, including a brief discussion of some general chemistry, the origin of chemically produced light, the effect of flame temperature and the role of color enhancers.

The last part of this paper discusses the psychology and physiology of color perception, including the classical theory of color perception and the potentially profound implications of Land's theory as it relates to color in fireworks. I suspect that most pyrotechnists, trying to improve their color effects, are spending their time working in the wrong area. They are working hard to squeeze the last little bit of improved color out of the chemistry and physics. I am convinced they would get a better return on their efforts if they studied and worked with the perception of color. I suspect that the most significant advance in pyrotechnics in this half century will not be the introduction of titanium or magnesium/aluminum alloys, but rather achievements resulting from improved understanding of color perception and work like that of T. Shimizu (1976, chapter 15) on the psycho-perception of fireworks.

3.0 The Physics of Colored Flames

3.1 The Nature of Light

The nature of light is one of the most important concepts presented in this paper. I will use an historical discussion of the evolution of the current theory of light to develop a comprehensive understanding of the nature of light.

3.1.1 Early Theories of Light

Before the seventeenth century, light was generally believed to consist of streams of tiny particles, or corpuscles, traveling between the source

of the light and your eye. According to this corpuscular theory of light, the way you saw things was by light corpuscles bouncing off objects and traveling to your eye. Being particles, light corpuscles must travel in straight lines unless acted on by outside forces, such as gravity. However, beginning in the mid-seventeenth century, experiments began to reveal properties of light that could not be easily explained using this corpuscular theory of light. In one type of experiment, it was noticed that beams of light often experience refraction (i.e., they are bent) upon passing between two different materials, for example, on passing between air and water (as in Figure 1). In other experiments it was discovered that light also experiences diffraction (i.e., it bends slightly around corners, as in Figure 2). These properties of light were most difficult to explain using the corpuscular theory of light. The light corpuscles were being bent out of their straight paths, yet there were no known forces acting on them. If, however, light were a wave motion, much like water waves, then the properties of refraction and diffraction would not only be allowed, they would be expected. Thus the wave theory gradually replaced the earlier corpuscular theory.

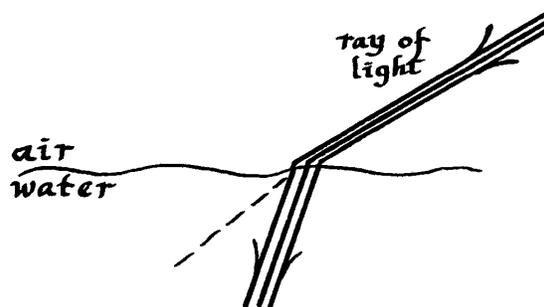


Figure 1. Refraction.

The wave theory looked pretty good for about 200 years, until near the end of the nineteenth century. The wave theory still served to explain all the properties of light concerned with its propagation from place to place. However, there were newly observed properties concerned with the ways in which light was emitted and absorbed that could not be explained if light consisted of simple waves. The first hint of a problem came when physicists attempted to explain the spectrum (i.e., the amount of light of various wavelengths) given off by a black body (i.e., a perfect radiator and absorber of heat energy). When such a black body

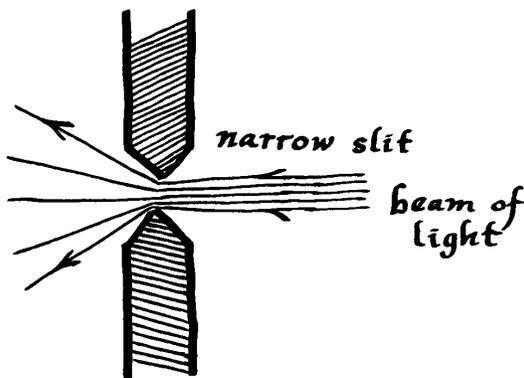


Figure 2. Diffraction.

is heated to a high temperature, it begins to glow, giving off visible light. When that light was analyzed in a precise manner, the experimental results simply did not agree with those predicted by theory (see Figure 3). Even after adjusting and readjusting the theory, it failed to explain the results. While this was worrisome, most scientists thought that the differences could be worked out within the wave theory.

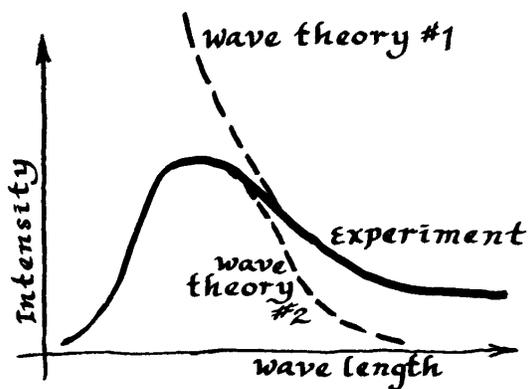


Figure 3. Black Body Spectrum.

The death blow for the wave theory (and what won Einstein a Nobel Prize) was the explanation of the photoelectric effect. It had been observed that under certain circumstances, electrons were emitted from the surfaces of metals when light shone on them (as in Figure 4). Unfortunately, those circumstances were not consistent with what would have been expected from the wave theory. It was observed that: 1) for all frequencies of light below a certain threshold, no electrons were emitted no matter how intense the source of light was

made; 2) as soon as this frequency threshold was exceeded, electrons were emitted instantly, even if the light source was of very low intensity; 3) above this frequency threshold, varying the intensity of the light source only affected the number of electrons emitted and not the energy carried off by them; 4) after allowing for the energy necessary to liberate the electrons, the energy carried off by them was proportional to the frequency of the light source. Some of these observations are illustrated in Figure 5.

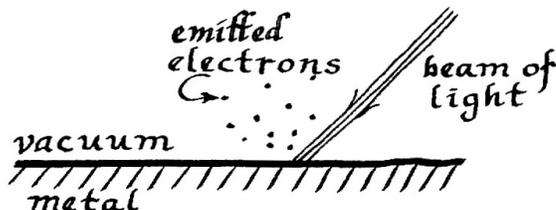


Figure 4. Photoelectric Effect.

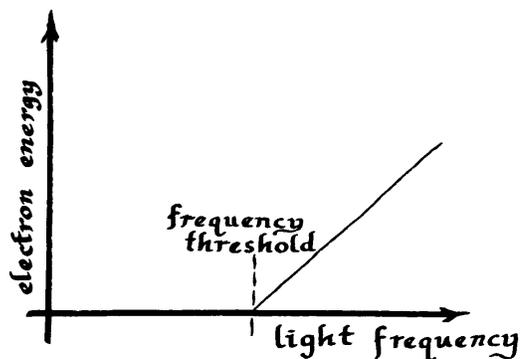


Figure 5. Photoelectron energy.

In the wave theory the amount of energy carried by a light wave was proportional to its intensity or amplitude (see Figure 6 for a graphic representation of some properties of waves). Thus if a certain amount of energy were required to liberate electrons from a metal surface, according to the wave theory, all that should have been necessary would be to increase the intensity of any source of light until electrons were emitted. This is contrary to what was observed. Also, the energy carried off by the electrons should have been proportional to the intensity of the light source and not to the frequency. The experiments with the photoelectric effect yielded results so far from those allowed by the wave theory that major adjustments had to be made to the theory of light.

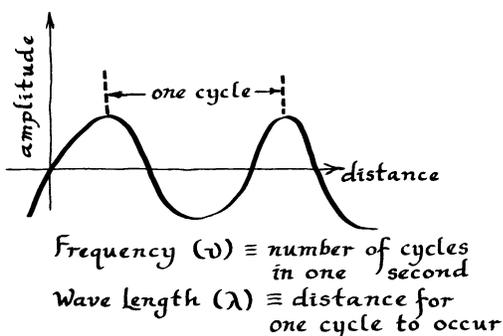


Figure 6. Waves.

3.1.2 Quantum Theory of Light

All the observations regarding the photoelectric effect are consistent with light being little packages of energy, and with the energy of each packet being proportional to frequency. If this were the case, the frequency threshold would represent the amount of energy necessary to free an electron from a metal's surface. If the frequency of light is less than this, none of the light packets have the required energy. If the frequency exceeds the threshold, then each of the light packets has sufficient energy to eject an electron and some liberated electrons should be observed even if the number of light packets (i.e., light intensity) were low. The intensity of the light source would affect the number of electrons emitted and the frequency would affect the amount of energy carried off by the electrons.

All this was consistent with experiments and might sound fine, but doesn't the idea of light packets sound a lot like light corpuscles? Well, it should, but with a new twist: remember, these packets now have a frequency, and therefore a wave length associated with them. What we have is something like a cross between a particle and a wave. That is to say, these light packets have some properties that are wave-like (they have a frequency and wave length) and some that are particle-like (they exist as discrete entities with discrete energies). What we have is the quantum theory of light (see Figure 7), in which: 1) light is emitted and absorbed as if it consisted of discrete entities, now called "photons"; 2) light is propagated from place to place as if it consisted of waves of a definite frequency and wave length; 3) photons carry amounts of energy that are proportional to their frequency. Quantum theory is the current theory of light and is the basis for our un-

derstanding of the atom as well. (NOTE: In the remainder of this text, photons are described rather indiscriminately, using their energy, frequency, or wave length. This is acceptable because their energy, frequency and wave length are uniquely related using the equations in Figure 8. After specifying any of the three properties, the others can always be calculated.)

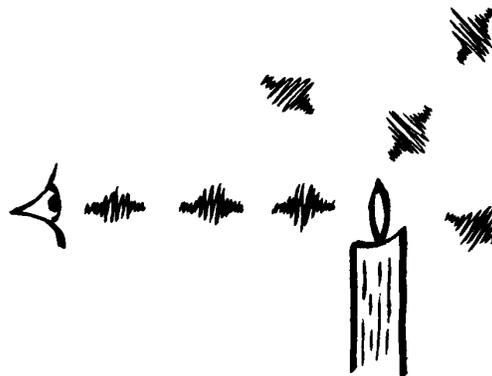


Figure 7. Quantum Theory.

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

$E \equiv$ energy	$C \equiv$ speed of light
$h \equiv$ a constant	$\lambda \equiv$ wave length
$\nu \equiv$ frequency	

Figure 8. Energy of Photons.

3.1.3 Definition of Light

Up to this point, we have not been very specific about our definition of light. The reason was largely one of convenience. Now that quantum theory and general nature of light have been introduced, it is time to be more specific. Among non-scientists, light is generally considered to be only that to which our eyes respond. So one possible definition of light is: those photons of the necessary wave length (or energy, or frequency) to invoke visual sensations. However, most people also know about invisible light as well, infra-red and ultra-violet light. Infra-red photons are longer wave length (less energetic) than visible photons and ultra-violet photons are shorter wave length

(more energetic) than visible photons. There are no fundamental differences between infra-red, visible and ultra-violet photons; they just have different wave lengths, and wave lengths are continuous (i.e., there are no wave length gaps between what we call infra-red, visible and ultraviolet photons). Then should our definition of light be made to include infra-red and ultra-violet photons?

The world is full of photons with wave lengths longer than infra-red (micro-waves and radio-waves are examples) as well as photons with wave lengths shorter than ultra-violet (X-rays and gamma rays are examples), see Figure 9. All these photons are fundamentally the same, and we would be justified in calling them all by the same name. However, for the purposes of this paper, we shall define light as only those packets of wave energy (photons) that are usually termed infra-red, visible and ultra-violet light.

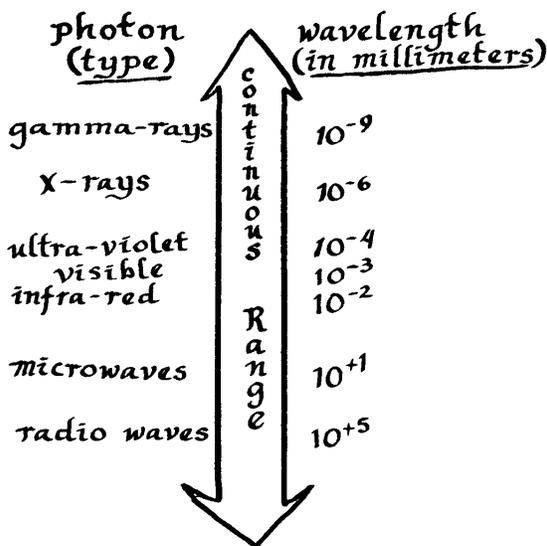


Figure 9. Continuous Range of Photons.

3.2 The Mechanism of Light Generation in Flames

Quantum theory is basic to our current understanding of physics for other reasons than its explanation of the nature of light. It plays a central role in almost every area of physics. In particular, it is necessary to have an understanding of quantum theory in order to be able to explain the mechanism through which light is generated.

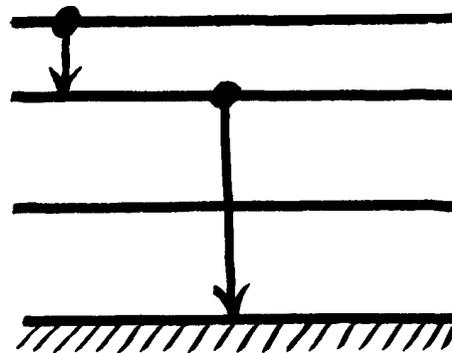


Figure 11. Energy Transitions.

3.2.1 More Quantum Theory

One of the major tenets of quantum theory is that “all bound systems are quantized”. Bound systems are those that are constrained to stick together in some manner. Some examples of bound systems are electrons whirling about an atom, the moon orbiting the Earth, and a weight swinging at the end of a string. In each case there is some force that holds the system together, electrostatic forces between electrons and the nucleus of an atom, gravity between the Earth and moon, and tension in the string attached to the weight. Quantum theory tells us that each of these bound systems is “quantized”. That is, these systems can only have certain allowed amounts of energy; they cannot have just *any* amount. Thus, the range of energy values for bound systems is not continuous; only specifically allowed amounts of energy are possible. It’s a little like climbing a ladder: you can stand on any rung you wish, but you can’t stand half way in between two rungs. If you try, you will fall to the next lower rung. It is the same way with these bound systems; each can have any of a number of allowed energies but none of the energies in between.

When a bound system has one of these allowed energies, it is said to exist in a particular “energy level”. Energy levels are often described using energy level diagrams like the one in Figure 10. The lowest energy level is called the ground state and those with higher energies are called excited states. The system being described in the energy level diagram can have energies corresponding to any of the allowed states but is forbidden to have any of those energies in between. If we try to give the system one of the forbidden energies, the sys-

tem will accept only enough energy to reach the next lowest allowed state. Bound systems also prefer to exist in the lowest possible energy states. If a system is given enough energy to reach a highly excited state, it will usually give up that energy, dropping to lower energy states.

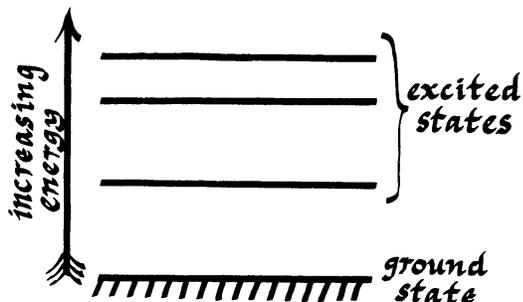


Figure 10. Energy Level Diagram.

When systems gain or lose energy, this is called an "energy transition". In energy level diagrams, energy transitions are shown as arrows between the energy levels involved. Figure 11 is the graphic representation of a bound system, originally in an excited state, losing energy through two energy transitions, dropping to the ground state. Note that it is not necessary for the system to pass through each intermediate energy state during an energy transition. In the case of the second transition in Figure 11, the system passes from the second excited state directly to the ground state, without passing through the first excited state.

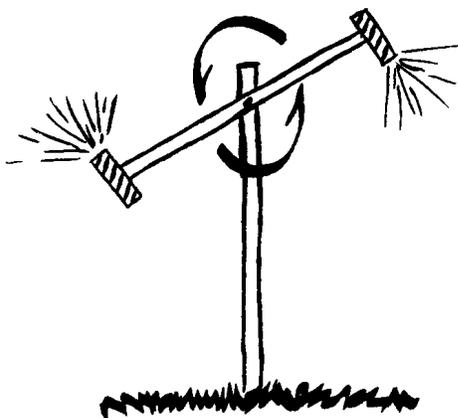


Figure 12. Pinwheel.

We have been talking about systems that have "energy"; but just how does that energy manifest itself? The energy can be in the form of motion within the system as in a whirling fan blade (kinetic energy) and it can be in the form of stored energy as in a compressed spring (potential energy).

Consider an example from pyrotechnics, that of a simple wheel as shown in Figure 12. The wheel is a bound system because it is constrained from flying apart by the stick connecting its two drivers. If quantum theory is correct, then the energy of this system must be quantized and can have only certain allowed values. In the case of a wheel, its energy is in the form of its spinning motion. Thus quantum theory predicts that only certain allowed rates of spinning are possible and that spin rates in between are not possible. This seems to contradict what we observe. In our everyday experience, it appears that the wheel can be made to spin at whatever rate we wish and that the rate of spinning varies continuously, not in steps. Is this observation reconcilable with what we know about quantum theory? Yes it is. It is not that the allowed energies and the steps between them don't exist: it is just that for objects as large as a wheel, the allowed energies are so very close together that we can't observe the steps even with our most sensitive instruments. For example, if the pin-wheel were stationary and a single particle of dust happened to fall on one of the arms, this dust particle supplies the pinwheel with a billion, billion, billion times the energy necessary to step up to the first allowed rate of spin. It's no wonder we can't observe the spin rate steps predicted by quantum theory.

Why bother with quantum theory if you can never hope to observe its effects on those objects in the world about us; why spend time trying to understand it? Well, in the sub-microscopic world of atoms and molecules, the steps between allowed energy levels can be enormous, and quantum effects are *very* observable. It is in this sub-microscopic world that light is generated. In order to understand and work effectively with light generating processes in pyrotechnics, it is necessary to have a general understanding of quantum theory.

3.2.2 Atomic Line Spectra

Now consider a more relevant example, that of an atom of hydrogen, Figure 13. The hydrogen

atom has a nucleus consisting of a single proton with a positive charge. About this proton is a single orbiting electron with a negative charge. The electron is constrained to orbit the nucleus by electrostatic forces of attraction resulting between opposite charges. Thus the atom of hydrogen is a bound system and its energy states will be quantized. If left alone, the electron in a hydrogen atom resides in the lowest or ground state. As energy is supplied to the atom, the electron can occupy higher excited states, moving to orbits that are farther from the nucleus. In pyrotechnics, this energy would usually be supplied by chemical reactions in a flame. To give an idea just how large a step exists between hydrogen's ground and first excited states, it would take a flame temperature approximately twice as great as that generated in a typical pyrotechnic flame to supply the energy for this transition. Unlike the fireworks wheel example, quantum effects in the hydrogen atom cannot be ignored!

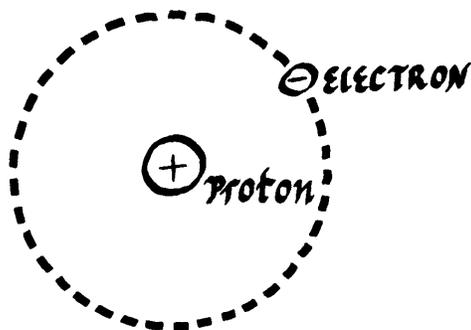


Figure 13. Hydrogen Atom

If a hydrogen atom had been energized to its first excited state, it could absorb additional energy with its electron moving to the second or even higher excited states. The energy required for this second transition is less than that required for the transition from ground to first excited state. However, it is more likely that the hydrogen atom will experience a transition back to its ground state. When this happens, the extra energy will usually be carried off in the form of a light photon. In the energy level diagram of Figure 14, the light photon emitted as the atom decays back to its ground state, is shown as a wavy arrow to the side. The energy of this photon is equal to the energy difference between the two energy levels involved in the transition, i.e., energy is conserved.

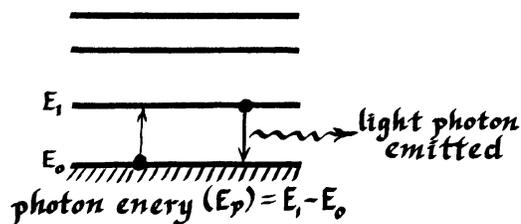


Figure 14. Atomic Light Generation.

If the hydrogen atom above had absorbed additional energy in a transition to its second excited state, it would have been faced with some alternatives regarding its transition back to the ground state. The transition could go directly to the ground state emitting a single higher energy photon, or it could be a two step process, passing through the first excited state, emitting two photons (see Figure 15).

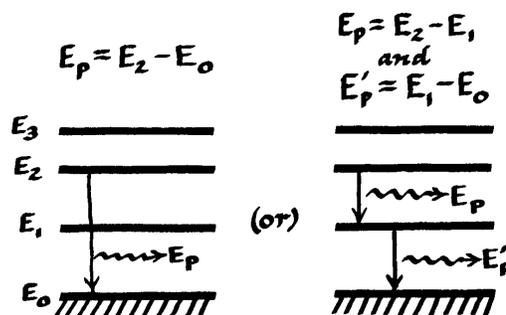


Figure 15. Atomic Transitions.

With the exception that the energies between allowed energy levels are greater, the example of hydrogen is typical of the first type of light production in pyrotechnics. Atoms absorb energy from a flame, causing electrons to occupy excited states; then the electrons drop back to their ground states generating light photons in the process. In each case, the energy of an emitted photon is exactly equal to the energy difference between the energy levels involved in the transition.

The energy levels of all atoms of a given chemical element have exactly the same set of precise energies. Thus, if a sample containing a large number of atoms of the same chemical element is excited sufficiently for electron transitions to occur, photons will be emitted, but only with certain specific energies. If a graph is made of the

number of photons emitted with different energies (see Figure 16), it will be observed that at most energies, zero photons are emitted. Only at a relatively small number of energies are photons observed. These photon energies correspond to the differences between allowed energy states for atoms of that chemical element. Had a different chemical element been used, the graph would appear similar; however, the energies at which photons are observed would be different. These graphs are representations of light spectra emitted by atoms and are usually referred to as “atomic line spectra”. They are called line spectra because all of the photons emitted by that chemical element have one of a set of very precise energies, giving the appearance of lines in the graph.

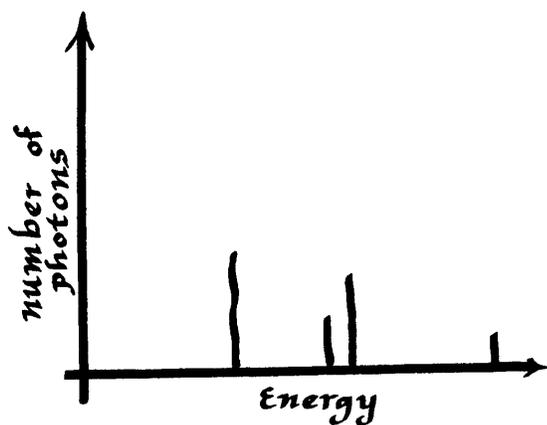


Figure 16. Atomic Line Spectra.

If the excited atoms emit some photons with energies that fall in the range of visible light, then an observer could see the emissions (provided they are intense enough). If these photon energies fall predominately in one part of the visible light spectrum, the emitted light appears colored.

The subject of colored light from atoms will be taken up again in the portion of this paper discussing chemistry. However, most useful sources of colored flame in pyrotechnics originate from molecules, not from atoms. It is therefore necessary to continue our discussion of quantum theory with a look at molecules.

3.2.3 Molecular Band Spectra

Molecules, like atoms, can be excited and experience electron transitions that result in photon emission. While the mechanism is the same, there is an important difference in the spectrum of pho-

tons emitted. The energies of emitted photons in atomic spectra have relatively few values giving rise to lines in the spectra; in molecular spectra, the energies of emitted photons have numerous values that cluster in groups giving rise to bands in the spectra.

Like the lines in an atomic spectrum, the bands in a molecular spectrum can be understood from quantum theory. Consider a simple molecule consisting of two atoms bound together. In addition to the electrons being bound to the atoms, the atoms are bound to each other in an arrangement that looks somewhat like the fireworks wheel discussed earlier (Figure 17). Like the wheel, the molecules can rotate. However, unlike the wheel with a rigid framework, the molecule is flexible; it can also bend and stretch, giving rise to vibrations as shown in Figure 18. Because the molecule is a bound system, these rotations and vibrations are quantized and can only take on certain allowed amounts of energy. The molecule can vibrate (or rotate) a little and be in a low energy state, or it can vibrate more vigorously and be in a higher energy state.

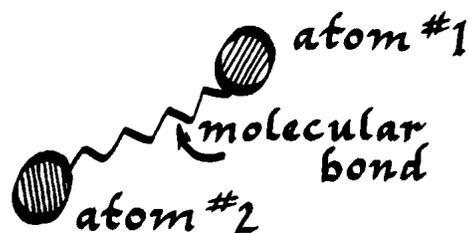


Figure 17. Simple Molecule.

Just as an energy level diagram can be drawn showing electron levels, energy level diagrams can also be drawn showing rotational and vibrational levels. However, the spacing between vibrational energy levels is much less than that between electron levels, and the spacing between rotational energy levels is even less than that between vibrational levels.

Like an atom, a molecule must always be in one of its set of allowed electron energy states, the ground state or one of its excited states. In addition, a molecule must also be in one of its set of allowed vibrational states and in one of its set of allowed rotational states. However, the molecule can have any combination of its allowed electron, vibrational and rotational states. The energy of the

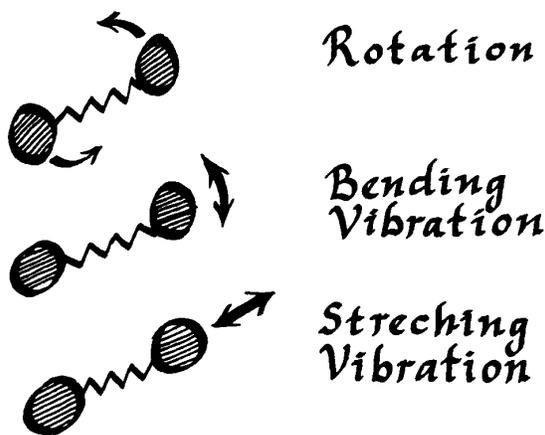


Figure 18. Molecular Motions.

molecule is the sum of its electron energy, plus its vibrational energy, plus its rotational energy. Thus an energy level diagram for a molecule will still have ground and excited electron states with spacings similar to those in an atom, see Figure 19-a. However, independent of its electron energy state, the molecule can exist in any number of vibrational states. Accordingly, added to each electron state in the level diagram will be a set of vibrational levels, each with slightly different energies. Figure 19-b is an attempt to show an exploded view of one electron level, Note that the electron level is broken into a number of closely spaced vibrational levels. Similarly added to each vibrational level is a set of rotational levels. Figure 19-c is an exploded view of a single vibrational level, Note that the vibrational level is further broken down into a set of rotational levels. The net effect is to have groups of very closely spaced energy levels, each group starting at the energy of an electron level.

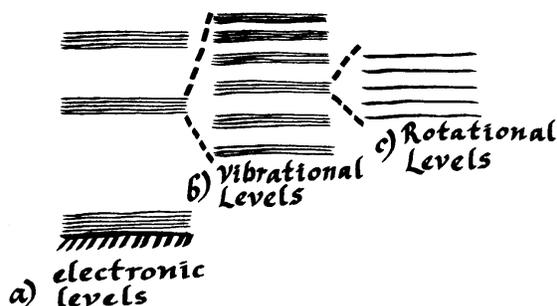


Figure 19. Molecular Energy Levels.

When a molecule receives energy and is excited, it can occupy any of the levels in one of these closely spaced groups. Similarly, when the molecule loses energy in a transition back to a lower energy state, the molecule can again occupy any of a large number of energy levels, see Figure 20. The energy of photons given off during such a transition to a lower energy state is still equal to the energy difference between starting and final states. However, because there are numerous, slightly different starting and final energy levels possible for this transition, a very large number of photon energies, differing only very slightly from each other, will be observed. The result is that molecules have band spectra (see Figure 21), while atoms have line spectra.

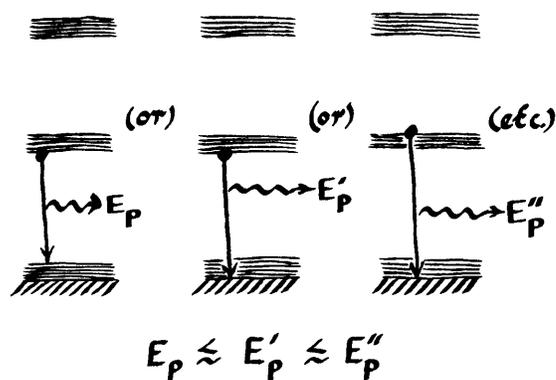


Figure 20. Molecular Transitions.

Just like atomic spectra, if the photon emissions from molecules fall in the range of visible light, they can be seen by an observer. If the emissions fall predominantly in one portion of the visible range, they will appear colored.

3.2.4 Continuous Spectra

In their relation to fireworks, the two light generating mechanisms discussed so far have the desirable characteristic of being able to produce intensely colored light. Unfortunately, there are two other light generating mechanisms that operate in flames that have a deleterious effect on color purity. This negative effect results from the generation of light photons with a continuous and wide range of energies throughout the visible spectrum. The effect of these continuous emissions is a washing-out of flame color, possibly ruining an otherwise excellent color effect. (NOTE: A thorough discussion of color is de-

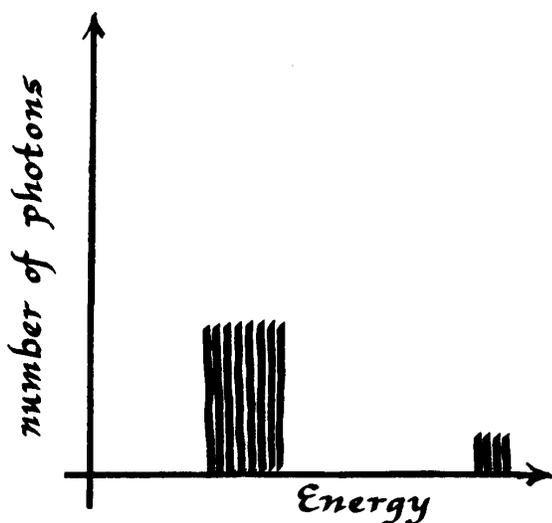


Figure 21. Molecular Band Spectra.

ferred until the next section of this paper. At that time the reason for this washing-out of color will be discussed.)

The first mechanism for generating a continuous spectrum in a flame can be understood using the same energy level diagrams that were used to explain atomic and molecular spectra. When discussing the level diagram for atomic hydrogen, it was mentioned that the separation between first and second excited electron states was less than that between the ground and first excited state. Similarly, the separation between levels continues to decrease as you go higher, until the separations between electron energy levels becomes microscopic at some limiting value. This limiting value is called the "ionization energy" for the atom (or molecule). If the atom acquires enough energy for one of its electrons to exceed this ionization energy, that electron is energetic enough to escape the atom completely, see Figure 22. Ionization of an atom is roughly like a space ship breaking out of Earth orbit. The result is a free electron and an ionized (charged) atom. What was originally a bound atomic system has become unbound and as a result is no longer quantized. Thus a free electron can take on any of the continuous range of energies, shown as the cross-hatched area, in Figure 23.

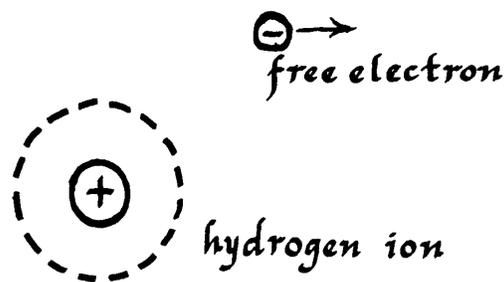


Figure 22. Ionization.

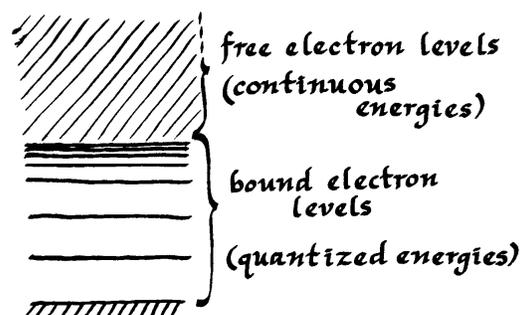


Figure 23. Free-Electron Energy Level.

Just as atoms do not normally exist in excited electron states (the first chance they get they undergo transitions back their ground states), free electrons and ions prefer to drop to lower energy states by recombining. Upon recombination, the excess energy is again carried off in the form of photons, but with one important difference: because the free electrons and ions started off as an unbound system, they did not have precisely defined energies before their recombination. Therefore, even though the energies of photons given off will still be the difference between initial (free electron and ion) and final (atom) energies, that energy will not be unique, see Figure 24. The result is not a line or band spectrum but a continuous spectrum of photon energies.

While on the subject of ions, it is worth pointing out that ions are still bound systems for those electrons that remain orbiting the ion's nucleus. Everything that was said about atoms and molecules still applies to electron transitions within atomic and molecular ions. It is only when ions recombine with free electrons that continuous spectra result, see Figure 25.

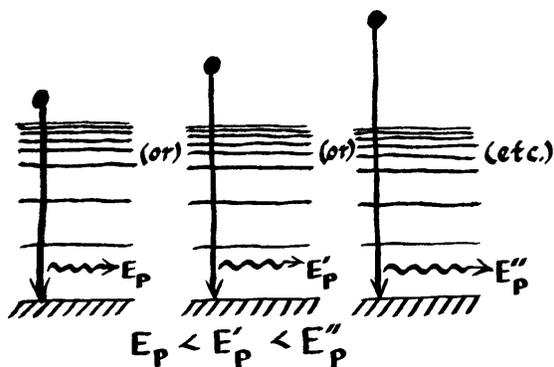


Figure 24. Ion Recombination.

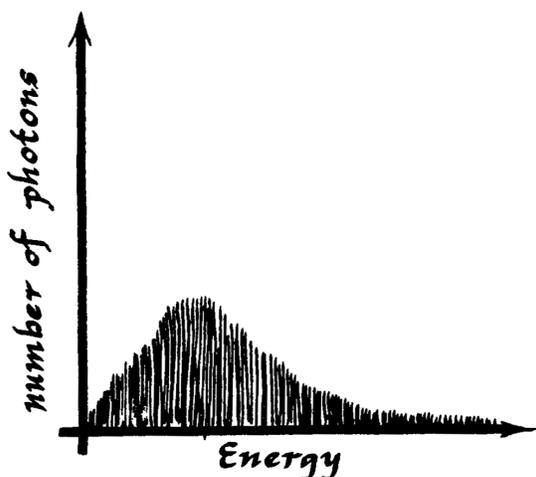


Figure 25. Continuous Spectrum.

The other mechanism by which continuous spectra are generated is incandescence. When any solid or liquid is heated to a high temperature, it will glow (remember black bodies in an earlier section). The object is seen to glow because it is emitting photons that are in the visible range. As the temperature is increased, the object glows brighter and the average energy of the emitted photons increases. In pyrotechnics, smoke particles and other non-vaporized material will incandesce in flames, producing a continuous spectrum, which can seriously wash out color.

In order to explain the physics of incandescence it would be necessary to introduce another area of quantum theory, called solid state physics. That would be a difficult exercise for the author and reader alike. Because the details of incandescence are not a particularly important topic, solid state physics will not be introduced.

Even the very tiny particles in smoke consist of billions of atoms bound together. When this is the case, it is no longer proper to think of the atoms as individual entities in the solid. It is the solid (or liquid droplet) as a whole that quantum theory treats. The net effect of having a system containing billions of atoms is a complete smearing out of identifiable energy levels for the smoke particle. In a way it is an extreme example of what happened in the molecule above. When we went from one atom to just two atoms in a simple molecule, we caused the introduction of many additional vibrational and rotational levels. When we now consider a smoke particle with billions of atoms bound together, the result is the introduction of billions of billions of additional levels, see Figure 26. When a smoke particle is thermally excited and when there are transitions back to lower states, it can assume any of the myriad of smeared-out states. The result is that the emitted photons can have essentially any energy whatsoever, creating a continuous spectrum.

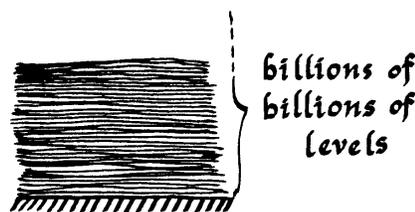


Figure 26. Smoke Energy Levels.

3.3 The Definition, Laws and Measurement of Color

In this section I will only deal with light's wave-like properties. Much of the discussion will concern the wave length of colored light sources. I will also discuss the laws of color mixing and the measurement of color. While recent theories of the perception of color may form a new basis for understanding the classical treatments given in this section, the classical approach is still in general agreement with observation and will provide a useful framework from which to discuss colored flames.

3.3.1 The Definition of Color

In the seventeenth century, Newton made the observation that a beam of white light falling on a prism could be made to separate into a continuous series of colors, now called the visible spectrum,

see Figure 27. While he was at a loss to explain the physical basis for his observations, his work laid the foundation for understanding color, and he developed the first laws of color mixing.

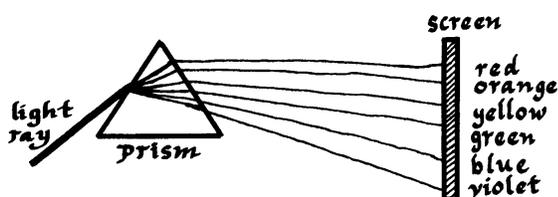


Figure 27. Newton's Observation.

The colors Newton saw in his experiments ran from violet (bent most by the prism) through blue, green, yellow and orange, to red (bent least). The colors were continuous, there were no gaps and they graded smoothly from one color to the next. If the colored light from the prism is made to fall on a strip of white material, we get a more conventional picture of the color spectrum, see Figure 28. Wiggly lines have been added to the sketch to denote the approximate limits to the various spectral colors. These wiggly lines are artificial and do not appear in a real spectrum. Wave lengths corresponding to the various colors are also included in the figure. The wave lengths are given in nanometers, or billionths of a meter.

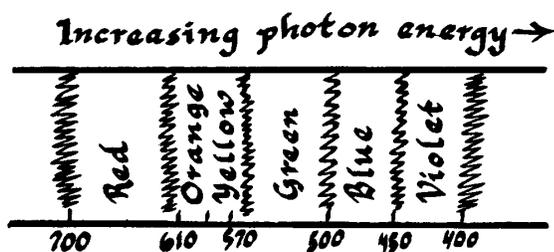


Figure 28. Visible Light Spectrum.

It is important to understand what the prism has done. It has not changed white light into colored light; the light that originally appeared white was already a combination of the different colors. What the prism did was to cause each color component of white light to be bent a different amount when passing through it. This caused the various color components to diverge from each other and fall on different parts of the screen. There is no single energy of light photons that will appear white to an observer. Whenever we see something

as white, it is because our eyes are receiving the proper combination of colored light to be mentally interpreted as white.

Beyond the short wave length limit of violet and the long wave length of red, Newton observed the spectrum to fall dark. These are the ultra-violet and infrared regions of the light spectrum. It is not that light photons do not fall in these dark regions; it is just that our eyes are not sensitive to light of these wave lengths.

For purposes of this paper, color shall be defined as “those visual sensations produced when viewing any combination of light sources having any combination of wave lengths in the visible region of the spectrum”. As such, color is a psychological reaction to a visual stimulus and only exists in the mind of the viewer. This subjective definition was chosen rather than a precise physical definition, because it is possible to produce most color sensations in many different ways, using different combinations of different wave length light. Accordingly, most colors are *not* uniquely quantifiable in the sense of being able to characterize color on a “*unique*” set of physical properties.

The above definition of color must seem rather unsatisfactory. Be patient—the reason for this imprecise definition will become clearer after discussing chromaticity diagrams and the laws of additive color mixing later in this section.

3.3.2 Flame Spectra Seen Using a Prism

Newton's prism was a rudimentary form of today's visible light spectroscopy, which can be used to analyze a source of colored light by separating it into its color components. It might be useful to consider what atomic, molecular and continuous spectra would look like with such a spectroscopy. In order to do this effectively, and also tie the discussion to what was presented earlier when discussing quantum theory, it is necessary to make a very important distinction: all photons have definite measurable energies. If they have a single energy that falls in the visible range, they can be seen by an observer and will appear colored. The color they appear depends on their energy. Low energy, visible photons produce a color sensation of red; high energy visible photons produce the color sensation of violet. Photons with energies in between will produce the color sensation corresponding to one of the other colors Newton saw using his prism. These colors are called “spectral colors” and they are special col-

ors, special because for them there is a unique relationship between color and photon energy. However, spectral colors represent only a tiny fraction of all possible colors. For the majority of color sensations, those produced when viewing a combination of different energy photons at the same time, there is no unique relationship between color and photon energy. This is because for all colors that are not spectral colors, the same exact color sensation can be created using an infinite number of combinations of different energy light photons.

Let me summarize that part of what I just said that is important for this section of the discussion. For spectral colors, those special color sensations produced by photons all having the same energy, a unique relationship exists between color and photon energy.

If the light coming from an atomic light source were made to pass into the spectroscope, photons with different energies (colors) would be separated. If they were projected onto a screen, they would appear as a series of colored lines separated by dark spaces. Figure 29 is an example of what might appear on the screen. Each colored line corresponds to one of the energy lines in the graph in Figure 16. In Figure 16, the length of the line was used to indicate the intensity of that energy photon. In Figure 29, each of the colored lines is equally long, and the intensity of each color line is determined directly by observing its brightness.

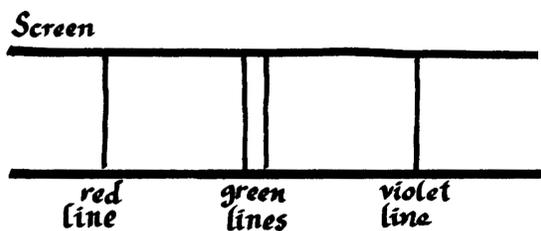


Figure 29. Atomic Line Spectra.

Figure 30 is an example of what might appear if we were observing a molecular source of light. In this case the spectroscope would produce bands of color with dark regions in between. These colored bands correspond to the bands graphed in Figure 21. If we were to observe an incandescent light source, emitting a continuous spectrum, the spectroscope would produce something like the visible light spectrum of Figure 28; various colors of light would fall throughout much or all of the

color spectrum and there would be no gaps between any of the colors present.

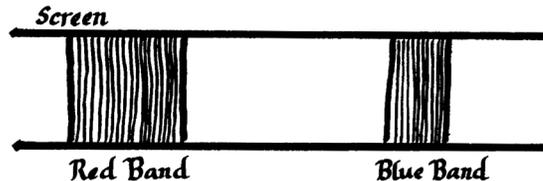


Figure 30. Molecular Band Spectrum.

3.3.3 Chromaticity Diagrams

Newton found that it was possible to generate a very large number of new colors, including white, by blending sources of the spectral colors: red, green and blue. In order to deal efficiently with this subject of composite colors, it was necessary to find some way of quantifying observations. An obvious possibility was to use a three dimensional graph (this page is a two dimensional surface). The approach would be to represent the colors produced in such a manner on a three dimensional graph in which each of the three axes corresponded to the intensity of one of the three primary colors. If this were done, each of the colors produced would correspond to a point in this three dimensional color space.

Fortunately, a much simpler, two dimensional method was developed to represent spectral and composite colors. This was made possible by the observation that if the brightness of all three primary light sources were varied proportionately, e.g., if the intensities of each source were doubled, then the composite color remains unchanged except for its brightness, which is also doubled. Thus, it is only the fractional intensity of the three primary colors that determines the composite color. In addition, it is only necessary to specify two of these fractions to completely describe the mixture. For example if a composite color is made using red, green and blue light sources, and you are told that $1/3$ red and $1/3$ green light has been used, then because the total must equal one, obviously the amount of blue light being used must also be $1/3$. A convenient method to represent color is just to specify two of the three primary color fractions, and this can be done using a graph in just two dimensions. When color fractions are plotted for all colors, the result is what is commonly referred to as a "chromaticity diagram", see Figure 31.

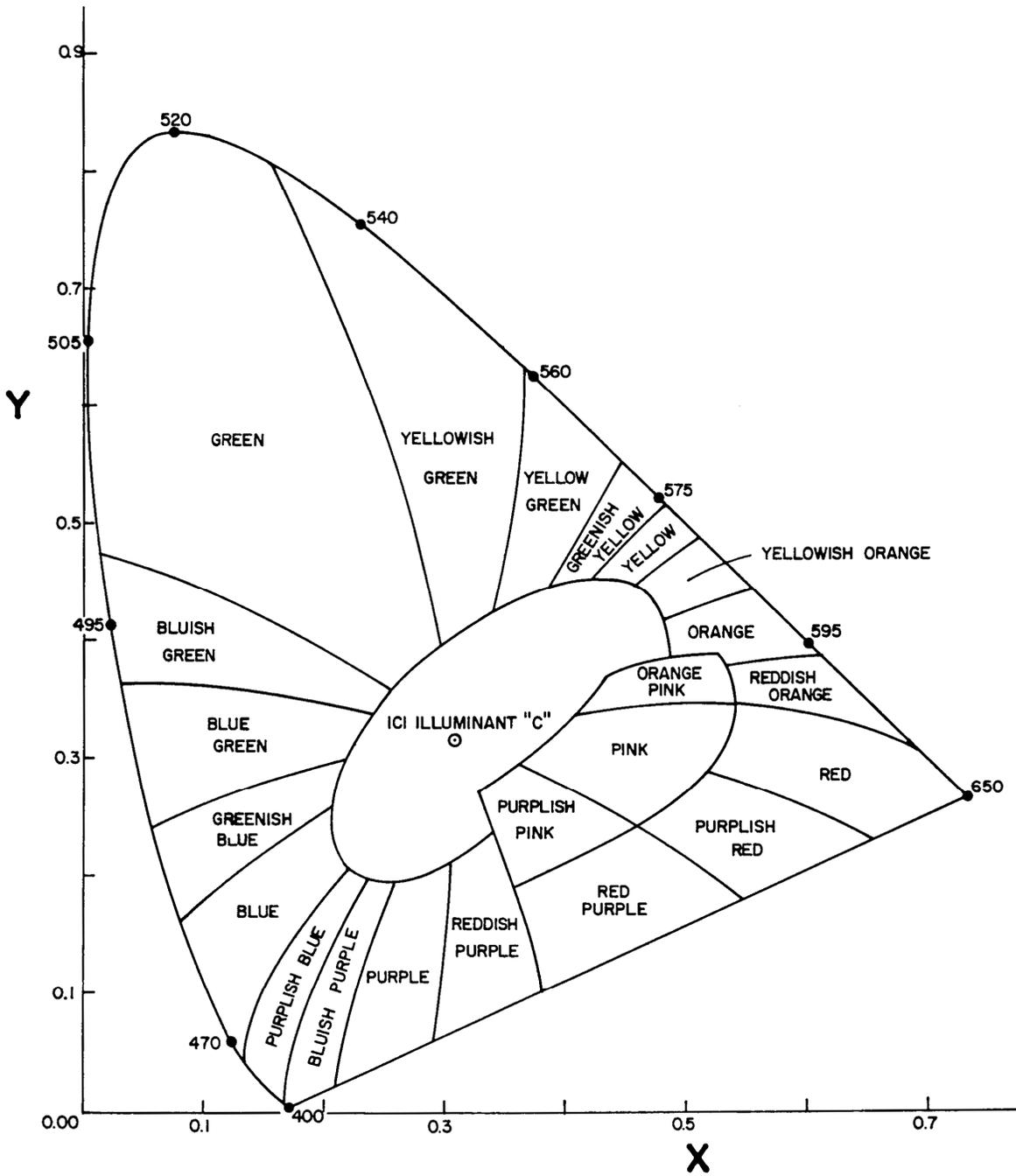


Figure 31. Chromaticity Diagram.

All possible composite colors fall inside the tongue-shaped color region of the chromaticity diagram. The pure spectral colors fall on the curved line surrounding the composite color region. Spectral wave lengths (in billionths of a meter, called nanometers) have been included for some of the color points along this spectral color line. The colors listed in the chromaticity diagram

of Figure 31 are those that a typical observer of the composite colors would call them. The colors grade gradually from one to the next. The lines separating each of the colors have been added as a convenience and serve to indicate the approximate boundary at which our typical observer begins to call the colors by some other name.

The shape and orientation of the color region depend on the choice of three primary colors. If negative fractions of the primary colors are allowed, e.g., $\frac{3}{4}$, $\frac{3}{4}$ and $-\frac{1}{2}$) then almost any three different colors make satisfactory primaries. In fact, even if we choose the spectral colors of red, green and blue, it is not possible to make all of the other colors without occasionally using negative amounts of the primary colors. On a mathematical level this is okay, but it is confusing conceptually. How can you use less of a primary color than none at all? That is what a negative amount represents.

In order to eliminate the necessity of negative color fractions and to standardize diagrams, an international commission on illumination was assembled in 1931. Their solution was to invent three new (unreal) primary colors. Remember, chromaticity diagrams were created just to make it a little easier to deal with the subjective science of color; there is nothing sacred about chromaticity diagrams or the primary colors on which they are based. If three slightly unreal primary colors will help to make color easier to work with, they should be allowed, providing everyone uses the same primary colors. The chromaticity diagrams in this text are based on these primary colors chosen by the 1931 International Commission on Illumination.

The point near the center of the chromaticity diagram labeled illuminant "C" is the color point for a standard light source called illuminant "C". This standard was chosen because it is a good approximation for average daylight and is now taken as the definition for white light.

3.3.4 The Classical Laws of Additive Color Mixing

For the most part, these laws of color mixing were derived as the result of subjective observation using people as scientific measuring instruments. Remember, color is a psychological response to a physical stimulus; it is in your mind and has no physical attributes that can be measured with scientific instruments. In effect, these color mixing laws are just a systematic expression of our everyday observation of color. As such, they have served us well. Recent work by Land (1974) has demonstrated that these simple laws are not always satisfactory. However, these laws will go a long way to help explain color in pyrotechnics and will be very useful when discussing

the chemistry of colored flames in the second part of this paper. Therefore they will be discussed here in some detail. In the third part of this paper, we will look beyond these classical laws of color mixing and will discuss some of the very exciting possibilities suggested by Land's work.

As you read the material in this section, you will need to refer to the chromaticity diagrams in the figures. For simplicity in these figures, the color information has been eliminated: thus, you will probably find it necessary to occasionally refer back to Figure 31 for that information.

The first of the classical laws of color mixing simply states that *every color is represented by a definite point in the color region of the chromaticity diagram*. All of the slightly different colors we might call green will have color points falling somewhere near Point "A" in the chromaticity diagram in Figure 32. Similarly, all light sources we should call yellow have color points somewhere near Point "B".

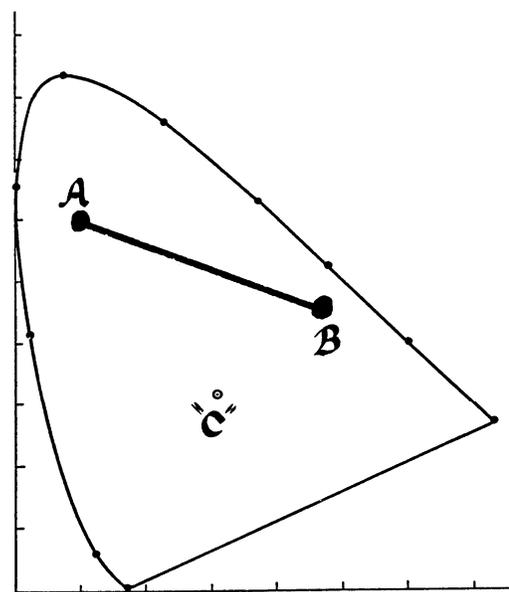


Figure 32. Color Points and Lines.

The second law of color states that *when two color light sources are added together in various proportions, the resulting color points will lie along the line connecting the original color points*. For example, if green and yellow sources of light, Points A and B, are mixed, the resulting color will always lie along the line AB. Depending on the relative amounts of green and yellow used, any color from green, through yellowish

green, yellow green and greenish yellow to yellow is possible. However, none of the colors not on the line AB are possible. It is not possible to make blue or red by mixing sources of green and yellow light.

The third law states that every color, except pure spectral colors, can be made using any of a large number of combinations of color sources, and that those composite colors will appear indistinguishable to an observer. For example, if it were desired to make white light (illuminant "C"), one possibility would be to mix bluish-green (color Point D in Figure 33) and pink light (color Point E). By varying the relative proportions of the two colors, all the colors along the line DE can be made. Observe that the color point for illuminant "C" falls on this line. Thus white light can be made, using sources of bluish green and pink light in the correct proportions. Other possibilities are to mix yellowish green and reddish purple (line FG) or purplish blue and greenish yellow (line HI) in the proper proportions. In fact, the number of possibilities is infinite. If observers, using only their eyes, compared the standard light source, illuminant "C", to each of the three composite sources just described, they would be unable to discern any difference.

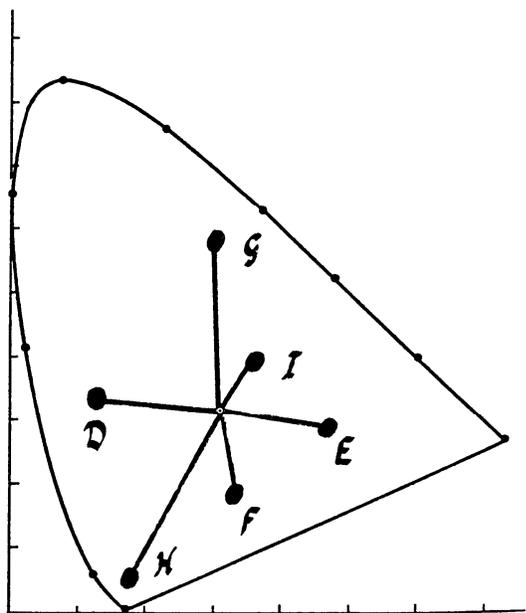


Figure 33. Color Combinations Producing White Light.

As an extension of the third law, if an additional source of colored light is added to a number

of different composite sources, each producing the same color point, then the final color points resulting from the combinations will all fall at the same place in the chromaticity diagram and each will appear identical in color. From the illuminant "C" example above, if a source of red light were added to each of the three composite sources resulting in color points at illuminant "C", in every case, the result would be the exact same shade of pink.

Using the laws of color mixing, it is now possible to demonstrate why the spectral colors red, green and blue can be used in combinations to make most, but not all, of the other colors. To do this, first consider a source of spectral blue light, color Point K in Figure 34. If spectral red (color Point L) is added to the blue, any of the colors along the line KL can be made. Next the red is "turned off". If a small amount of spectral green (color Point N) is turned on while the blue is turned down a little, the color Point M, on the line KN, can be reached. If red is again added to the green and blue combination, any of the colors along the line ML can be made. Now, if red is turned off again and a little more blue is replaced by green, color Point O can be reached. If once again red is added, any color along the line OL can be made. If this process is continued, eventually the blue light will be completely replaced with green. When this happens and red is added, any of the colors along the line NL can be made. Thus, it should be clear that all of the colors inside

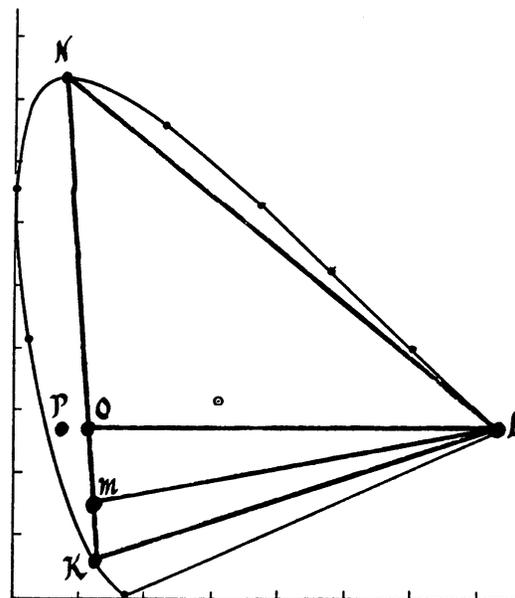


Figure 34. Primary Color Mixing.

the triangle KNL can be made using combinations of the spectral colors red, blue and green. These colors, inside the triangle KNL, constitute most, but not all, colors in the chromaticity diagram. Consider the color at Point P. The closest you can approach it using blue and green is the color Point O. When red is added, color points along the line OL will be reached. The more red that is added, the closer the composite color points move toward the red color Point L. Thus, adding any red at all takes us farther from the desired color Point P. In order to reach Point P, it would be necessary to add less than no red at all, i.e., a negative amount of red. From a practical standpoint, this is impossible. The color at Point P is one of those that cannot be made using spectral red, green and blue; similarly, none of the colors outside the triangle KNL can be made using these primary colors.

3.3.5 The Measurement of Color

The basis for the measurement of color follows from the third law of color mixing, from something I will call the principle of equivalent color. Even though there are many ways of combining colored light sources to produce the same color sensation, they are all equivalent as seen by an observer. Therefore, a precise physical description of any of those methods producing the color sensation will serve to define the color. For example, we previously described three different combinations that created the color of illuminant "C". If I precisely describe any of these methods, then I have defined the color point for illuminant "C". This process for defining (measuring) color is satisfactory, but would be improved if the method were completely standardized.

The standard method is based on the observation that most color points on the chromaticity diagram can be reached using a combination of white light (illuminant "C") and one of the spectral colors. For example, the color Point P in Figure 35 can be reached using a combination of white light and the spectral color with a wave length of 490 nanometers. If the wave length of the spectral color and the percentage of the distance along the line from illuminant "C" to the spectral color are specified, then the color point is completely defined. The wave length of the spectral light used is called the "dominant wave length". The percentage of the distance along the line is called "purity". In this example, the domi-

nant wave length of color Point P is 490 nanometers and its purity is 85%.

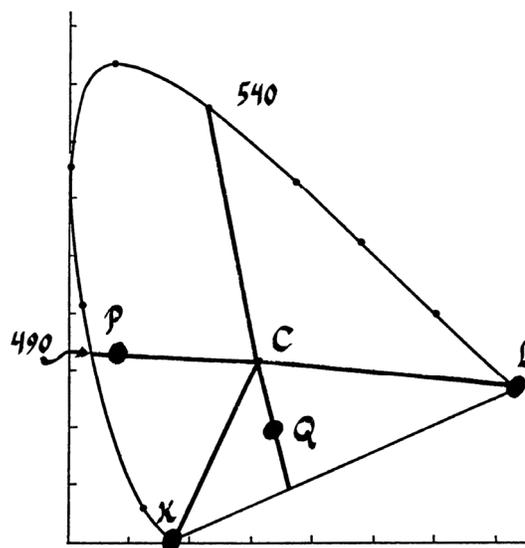


Figure 35. Measurement of Color.

This standard method of measuring color must be modified slightly if colors in the triangle CKL (Figure 35) are to be treated. These colors (sometimes called nonspectral colors) cannot be made by combining white light and one of the spectral colors. Consider the color Point Q; this color does not have a "dominant" wave length as described above. However, what is called its "complementary" wave length can be found by extending the line QC until it intersects the line of spectral colors. In this case, the color Point Q has 540 nanometers as its complementary wave length. In order to indicate that this is the color point's complementary wave length, the prefix C is added, i.e., C-540. The purity of the color is determined as above and is the length of the line CQ, expressed as a percentage of the distance from Point C to the line KL. Thus, the color at Point Q would be measured as having a dominant wave length of C-540 nanometers and a purity of 50%.

Colors are completely defined by specifying their dominant wave length and purity. However, colored light sources have another attribute that must be specified, that of brightness. The brightness of a light source is measured as luminous flux, or for the purposes of this paper, intensity. Light sources in pyrotechnics are completely described using only dominant wave length, purity and intensity. None of the other terms such as hue,

saturation, chroma, etc. are necessary (or even useful) in pyrotechnics.

3.4 The Physics of Colored Flames, Applied

In this last section, before taking up the chemistry of colored flames, it is appropriate to apply the physics already discussed in pyrotechnics.

In an earlier section of this paper, it was said that atomic line spectra have the desirable characteristic of being able to produce deeply colored flames, and this is true. Consider the hypothetical case of atoms of some chemical element that produce spectra with only one spectral line falling in the visible region. In this case the color point corresponding to electronic transitions in this atom will fall somewhere along the outer edge of the color region of the chromaticity diagram. This spectral color, by definition, has a purity of 100%. If this is the only light source in the flame, the flame will be very deeply colored. The particular color generated will depend on the wave length (energy) of the spectral line. In this example, our spectral line, Point A in the chromaticity diagram in Figure 36, has the dominant wave length of 450 nanometers. Unfortunately, there are two things wrong with this hypothetical case. First, I do not know of any atoms that have only one spectral line falling in the visible region. Second, in a pyrotechnic flame, there will be many differ-

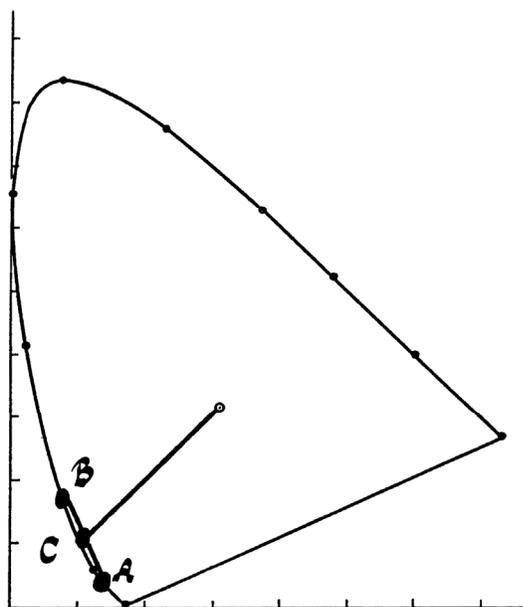


Figure 36. High Purity Example.

ent atomic species present, each contributing their own spectral lines.

Let us examine the effect these added spectral lines have on our hypothetical colored flame with 100% purity. We shall start by adding just one additional spectral line, color Point B in Figure 36. This second spectral line has a dominant wave length close to that of the first spectral line. The composite color must lie somewhere along the line AB connecting the spectral color points in the chromaticity diagram. The exact position of the composite color will depend on the relative intensity of the two spectral lines. If we assume the intensities are equal, the composite color point will lie at Point C, midway between Points A and B. The composite color will still be very pure, about 97%, in this example. The most noticeable effect will be a slight shift in dominant wave length to a value between that for A and B. To an observer, the effect will be a slight change in color, but the flame will still be seen as an intensely deep color. If, on the other hand, the second spectral line we added had a dominant wave length quite different from the first, then real problems can result. Consider the case where the added spectral line (Point D in Figure 37) has a dominant wave length of 560 nanometers. If this spectral line has only one-tenth the intensity of the first line, the composite color point will fall at

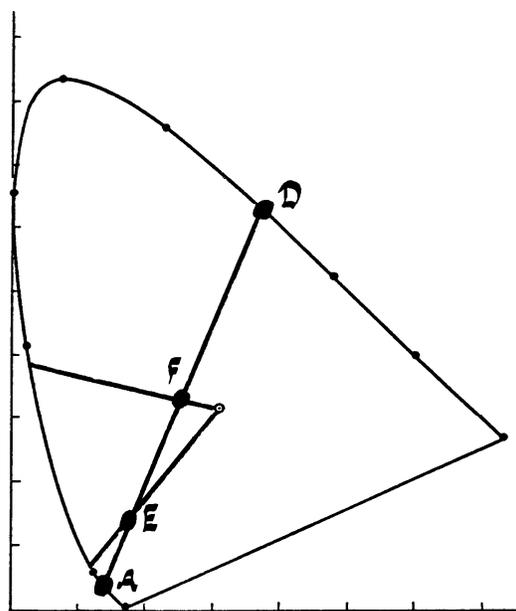


Figure 37. Low Purity Example.

Point E. Color Point E has about the same dominant wave length as in the high purity example in Figure 36. However, its purity has dropped to only 70%. There will be a slight change in color to an observer, similar to that in the first example, but the color will appear noticeably washed-out. Had the second spectral line been equal to the intensity of the first, as it was in the high purity example above, the composite color would have the color Point F. The dominant wave length of this composite color has changed greatly, and its purity is only about 20%. This light source will appear almost pure white to an observer, a devastating loss of flame color.

In the real world, pyrotechnical flames have atomic and ionic species producing a lot more than just two spectral lines. Thus, it is understandable why it is difficult to produce deeply colored pyrotechnic flames. All one can hope for is that the collection of spectral lines produced will tend to predominate in one spectral region, giving reasonably pure colors. In practice, colored pyrotechnic flames have color points falling somewhere inside the shaded doughnut shown in the chromaticity diagram of Figure 38.

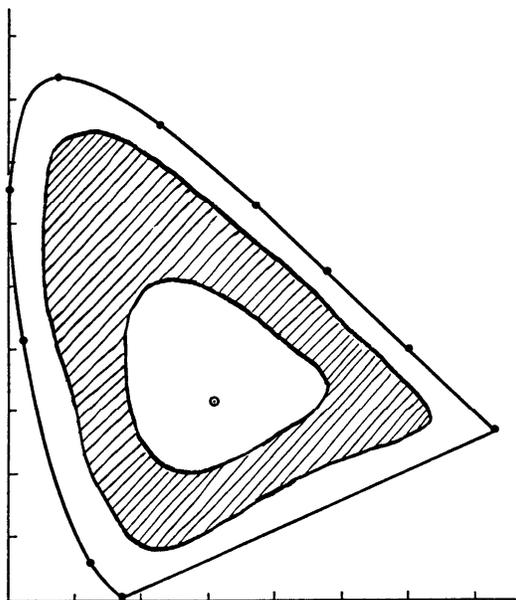


Figure 38. Colored Pyrotechnic Flames.

Thus far we have discussed atomic line spectra; however, molecular band spectra are much more common in pyrotechnic flames. A molecular band spectrum with just a single band will produce a deeply colored flame just as in the high

purity example of Figure 36. Remember that a molecular band is just a collection of closely spaced lines that give the appearance of being a continuous band. On a chromaticity diagram, it is as though there were a large collection of color points in one spectral region. The collection of equally intense color points running from 450 to 480 nanometers, shown in Figure 39, will produce a composite color with the dominant wave length of about 470 nanometers and having about 98% purity. Thus molecular bands can be treated just the way that atomic lines were in the examples above, i.e., a molecular band can be treated as if it were an almost pure spectral line with its dominant wave length about midway through the band. Everything that was said above for atomic line spectra, applies equally to molecular band spectra or to mixtures of atomic and molecular spectra. The important thing to remember is that the wider the molecular band, the less pure (more washed-out) the color will appear.

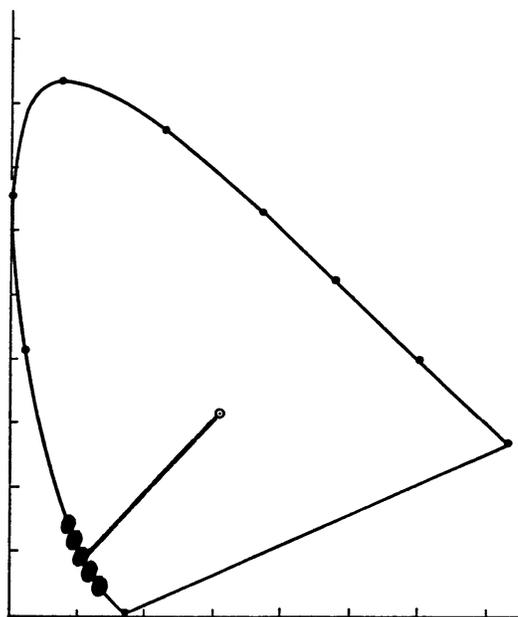


Figure 39. Molecular Band.

The next topic to consider is that of continuous spectra. These can be treated as nothing more than extremely wide bands. However, because of the extreme width, there can be a tremendous loss of purity. Consider the example of a continuous spectrum with equal intensity throughout the visible region. This would result in a composite color Point G in Figure 40, not far from the white color point of illuminant "C". If the continuous spec-

trum is generated as the result of incandescence, the composite color point would lie somewhere along the line GH. Its position along the line depends on the temperature of the solid or liquid material that is incandescing. It is obvious why sources producing continuous spectra can be so detrimental in pyrotechnic colored flames: they often produce nearly white light, and any white light added to colored flame reduces its purity, appearing as a washing-out of color.

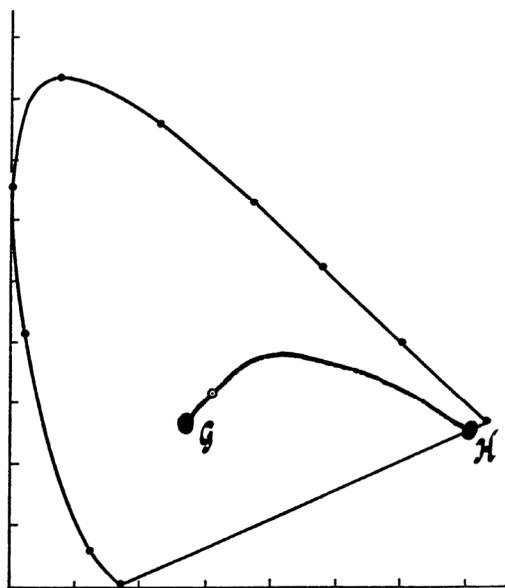


Figure 40. Continuous Spectra.

Finally, consider the case of purple colored flames. Any pyrotechnist will tell you that really good purples are very difficult to produce. The reason should be clear after studying a chromaticity diagram. In order to produce a deeply colored purple flame, it is necessary to generate a composite color with its color Point K inside the shaded region shown in the chromaticity diagram in Figure 41. To accomplish this, you need to mix spectral lines from the extreme opposite ends of the color spectrum, Points I and J. Finding the red source is fairly easy but finding an intense violet line (not blue) is tough. An even tougher problem is that the addition of even a small amount of green or yellow will move the composite color point out of the intense purple region with a rapid loss of purity. Suppose we have a source of green light, in our otherwise excellent purple flame, with a relative intensity only one-fourth that of the purple composite. The result will be the new color

Point M. To an observer, this will appear white, a totally washed-out purple. This combined set of requirements, two-thirds violet light plus one-third red light with very little else in the flame, is really tough to achieve. We will take up the subject of purple again at the end of the chemistry section of this paper.

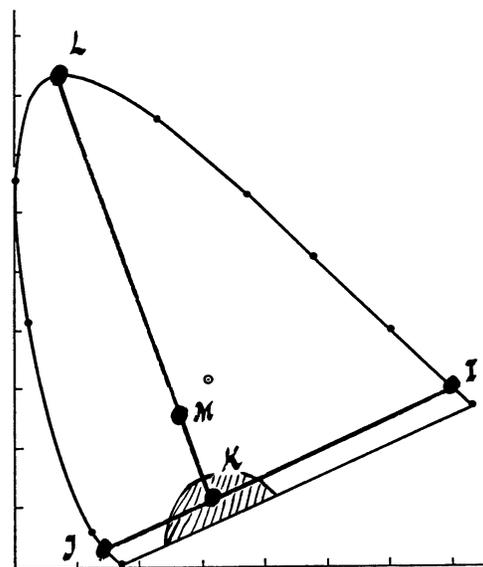


Figure 41. Purple's Tough.

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END OF PART I