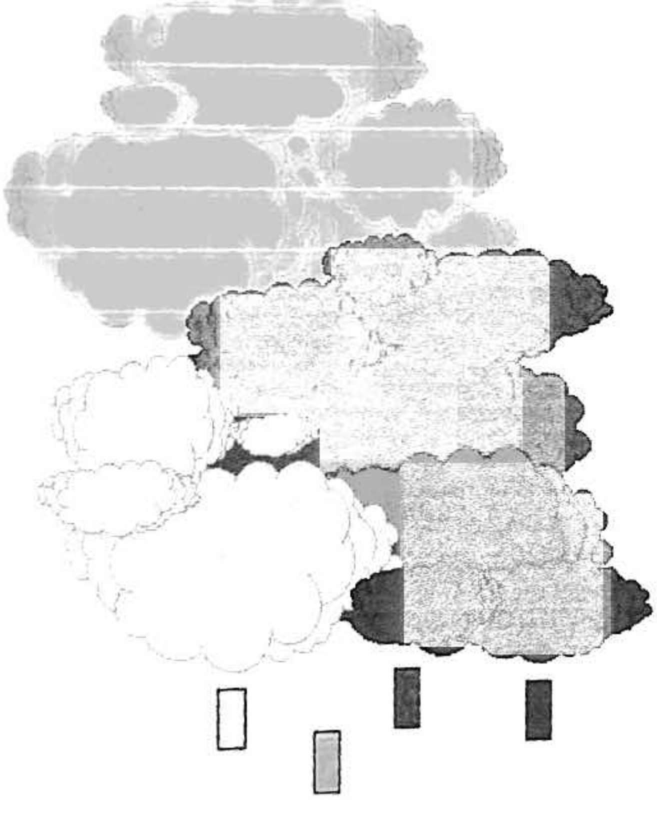
SMOKE GENERATION

TACTICAL ✳ SURVIVAL ✳ CIVILIAN

BASIC INGREDIENT STUDY, CONSTRUCTION AND USE



COLOR SMOKE

WHITE SMOKE

MILITARY HC

RODENT CONTROL

INSECT / PEST CONTROL

VOLATILIZED LIQUIDS

EXPLOSIVE SMOKE

COMPOSITE SMOKE

PELLET & GRANULATIONS

AN ILLUSTRATED STUDY OF SMOKE GENERATING COMPOSITIONS AND BASIC CONSTRUCTION TECHNIQUES

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PREFACE

This is the ***second*** writing in book form from a series of earlier papers and new information that represents many hours of designing and testing various devices using dozens of smoke producing materials and chemical supplies readily available to the hobbyist.

The project was taken as an effort to satisfy countless requests from the growing number of those, both novice and professional alike, who require reliable, tested information on pyrotechnic smoke production. Much of the literature available on the topic give limited information on construction techniques and list chemical candidates not readily available to the public or of a source not consistent to practical economical construction.

Our approach was to study basic procedures and various compositions, test them and adjust or weed out those not in favor of our objective and with them, those that include complex procedures or materials not generally available. As standard procedure, we include a list of possible ingredients, both smoke and gas producing, that can be used to decrease, increase or generally improve smoke generation. We also give results of burn testing individual components for visual assessment of possible use.

Information, procedures and results given in this text are by no means complete and final - nothing is set in stone. The study represents *only* the results of limited tests based on the somewhat limited resources available to the average hobbyist. Quality control and good resources and equipment will yield the best results. Apply them to the best of your ability.

Our approach and experiments were performed with the amateur in mind. We list technical information on ingredient candidates that may be applied to improve upon the compositions and devices to suit particular applications. Those experienced in the procedures can develop their own ideas and tooling befitting applications not particularly outlined in the text.

As per our tests, the results of our labors are listed and the reader/user must draw his/her own conclusions as to the fitness of use of the material and information supplied and draw a conclusion as to their application.

As we cannot control the use of this information and the quality of the equipment, chemicals or procedural techniques used, results may vary slightly from user to user. This is normal and may be remedied through quality control and patience. We express no warranties of safety or fitness of use for the information listed and the user assumes all risks and responsibilities associated thereof.

Experiments ***must*** be done with patience and a complete understanding of the chemicals, materials and procedures. Read and familiarize yourself with the information for each composition and device *before* you attempt to duplicate the exercises. Equip yourself as outlined and follow all safety procedures discussed. Always record your steps and the results of your tests as you proceed for future reference - right or wrong. Keep the information in a folder and review it from time to time when designing similar formulations or duplicating others. You will find this information invaluable as reference.

This material is for informational purposes only. It is based solely on the author's experiences using tools and procedures not necessarily explained in great detail. All risks regarding the use of this material are the reader/user's sole responsibility! In using this material, the user agrees to hold harmless the author, seller or any in part thereof for any claims, alleged or proven, damages, injuries, costs, losses or expenses resulting from the purchase and/or use of the information.

Any use of this material should only be attempted by persons 21 years of age or older fully cognizant of the nature of the chemicals, compositions and devices discussed. Do not proceed unless you fully understand what you have read and know how each chemical must be handled. Always remember to observe safety rules and conditions upon starting and secure proper permits required should there be any.

WARNING

Compositions and devices discussed herein may be dangerous to formulate, assemble and use. Utmost caution and proper safety practices must be observed at all times. Pyrotechnic compositions discussed herein may be sensitive to heat, friction and impact with those containing chlorates leading the list.

Whenever using chlorates, be very careful to avoid friction during the mixing process and never mix them with sulfur, sulfides, sulfates or antimonies. The resulting compound is extremely sensitive to heat, friction, impact and pressure. The liabilities generally outweigh the assets with these mixtures, however, used in compliance, chlorate mixtures may be used and stored with relative safety. **Never grind, pound, pulverize or compress mixtures containing chlorates!**

As with most any pyrotechnic composition or device, the compounding and construction of pyrotechnic mixtures and devices should be approached with caution! Their manufacture and use may be neither predictable nor completely reliable to operate as intended. The use of quality materials and a properly equipped work space is mandatory for safety and good results.

The procedures and results listed herein are that of the author's experiences which may not be outlined in great detail and therefore should not be construed as completely safe manufacturing practices.

As with any pyrotechnic mixture and/or device, smoke generating devices produce heat and flame during combustion. Discretion must be used to evaluate the surrounding area they will be used in to avoid spot fires. Used as cover smoke and thrown into dry grass or other combustible debris is a gamble at best.

BASIC SAFETY PRECAUTIONS

1) Always wear safety goggles, rubber gloves and respiratory protection (dust mask) during all operations.

2) Never smoke during operations or mix/prepare compositions near sources of heat or flame (including pilot lights). Always work in a well ventilated area.

3) Never grind or pulverize different classes of chemicals together - always separately. **Never grind oxidizers with any other chemical, metal powder or composition!**

4) Mixing should be accomplished by sifting several times through a clean 15 to 30 mesh brass or aluminum screen (these are non-sparking) followed by gently rolling / shaking in a clean plastic container with snap-on lid.

5) All mixing and production hardware should be plastic, glass, wood, brass or aluminum and properly grounded using a woven wire mesh grounding strap or similar. Any and all electrical equipment **must** be grounded in this manner as well as any large metal storage drums being used. Never use iron, steel or their alloys for mixing purposes.

6) Never prepare more composition than you intend to use at a time. Mixtures should never be "stored" in an uncompleted form. In unprotected dry form, many ingredients may be hygroscopic - that is to say, they will absorb moisture from the air causing degradation and poor performance. Use completed devices as soon as possible. Humidity, temperature, geographical location, storage duration and conditions all have adverse affects on pyrotechnic compositions and devices with spontaneous combustion during storage always a possibility in extreme conditions.

7) Always clean tools and equipment <u>before</u> a moist or uncured material has a chance to dry or cure. Dry / cured materials are much harder to remove (if at all) and are much more sensitive to heat and friction and therefore near impossible to remove safely and without damaging tools.

8) Always store chemicals, compositions and completed devices out of the reach of children at all times. Oxidizers and flammable chemicals and materials should be stored separately.

TERMS RELATIVE TO THIS TEXT

Carcinogenic;	Agent(s) or media that is known to cause various cancer(s).
Composition;	Mixtures of various components blended to a homogenized state.
Endothermic;	Chemical changes which absorb heat.
Exothermic;	Chemical changes which produce heat.
Granulation;	Refers to the particle size of individual ingredients or of composition screen kneading to obtain particular particle size(s) or granules.
Hygroscopicity;	The ability or rate of a substance to absorb moisture over others.
Stability;	The ability to retain intended properties in prolonged storage or of use under universal conditions.
Sublime;	To convert a solid substance by heat into vapor and upon cooling, condensing into a solid form (smoke particle formation).
Vaporize;	Convert from a solid or liquid to a vapor or gas.
Volitilize	Convert from a solid form to a vapor or gas.

BASIC THEORY AND USE

SMOKE PRODUCTION

Reliable, dense smoke formation as discussed herein can be more of an art than science. It involves the sometimes difficult combustion, incomplete combustion or sublimation of ingredients to produce gas and solid smoke particle formation.

The term "smoke" or "smoke formation" relates to the formation and suspension of fine solid particles in air. The production of *solid* particles create a higher density cloud which is different from liquid particles suspended as "fog" from aerosols. Here, the liquid particle aerosols are much lighter and smaller in particle size which disperse in air more rapidly than do solid particles.

Smoke production is tailored to the particular application in demand which will range from simple firework devices for amusement to high volume tactical designs to obscure troop and armament movement and signaling/survival applications. Other designs would include rodent control and insecticides, theatrical effects, rocket and missile tracking, mortar and artillery range-finding, etc..

This text will study candidate materials, their function, how to change desired effects by adjusting particle sizes, grain shapes and chemical percentages as well as ignition and propagation.

PROCESSED SMOKE CLASSIFICATIONS

1) ***Combustion;*** The high heat burning of compositions forming gas which, upon contact with the moisture in the air, forms solid particles. Example; hexachloroethane or ammonium chloride compositions form vapor chlorides of zinc, aluminum or other that react with moisture forming white smoke. A second is nitrate/sulfur compositions that depend on combustion to reduce the materials to their by-product gasses and residual solids forming the smoke cloud. This type does not necessarily depend on moisture for smoke production and is usually an off-white color. We should note that most pyrotechnic smoke formulations depend on the moisture content in air to create the dense particle formation. The higher the humidity, the more dense the smoke cloud.

2) ***Incomplete combustion;*** Smoke generated from imperfect combustion of hydrocarbon compositions. An example here is carbon/soot produced from naphthalene, anthracene, asphaltum or rubber compounds. This type of smoke is black in color.

3) ***Sublimation / volitilization;*** Smoke produced from a vaporized organic dye. An example is organic or aniline dye or compositions employing sulfur that are volatilized by a low heat reaction of combustible fuel(s) forming solid particles that attract moisture in air forming the desired color smoke.

4) ***Combination reactions;*** A few compositions employ a combination of reactions to create smoke particle formation. In one case, a hydrocarbon / chloride structure utilizes incomplete combustion, partial volitilizing role combining soot with vapors of chloride (acting as the colorant) producing white smoke in air. Another is an oxidized sulfur / fuel mixture in which combustion of a fuel causes sulfur to both sublime and combust producing solid smoke particles attached to gaseous products including carbon dioxide and sulfur dioxide. This type of smoke is typically used to control insects, rodents and other harmful pests in greenhouses and as mouse, mole and gopher control.

GRAIN FORMATION CLASSIFICATION

A) **Solid;** This type utilizes compression to form a solid pellet, stick or cannister known as the *grain.* Ignition of a pressed grain requires an adhesive prime mixture spread over the entire exposed surface or end grain. Solid devices of this type are generally long duration and relatively low smoke production used for checking wind drift, wind tunnel use and pest control when an additional insecticide component is added. An example composition would include nitrate / sulfur or of a carbon smoke formation from incomplete combustion. Phosphorous compositions also figure into this classification.

B) **Cored;** Grain formation of this type utilize a ram with coring spindle to compress the composition leaving a core for increased surface area of burn and dramatic volumes of smoke. The device is ignited at the bottom of the core (primed) where smoke output can be controlled by both depth and diameter of the core itself. Examples of this type include all four classifications listed above and color smoke devices.

C) **Powder;** The most common device using loose powder compositions are those produced for the consumer fireworks trade. They employ a small paper can loosely filled with the composition and fused with either safety fuse or a pull wire friction igniter (the latter being used by outdoorsmen for signaling and survival applications). This type of smoke composition packed loosely contains enough air space between the particles to provide an increased surface area of burn and subsequent satisfactory smoke volume. If color smoke compositions are used in this manner, the formulation must combust at a low heat and employ candidate materials that leave little or no ash to trap the subliming dye particles which would result in poor color quality.

UNDERSTANDING BASIC OPERATION

Smoke production has for years been a topic of great intrigue to civilian, industrial and military interests. Smoke generated as a product of solid and/or liquid combustion or of a by-product nature from industry is generally considered pollution and costly steps to control it are implemented. Smoke compositions designed for use in the pyrotechnics industry are quite another story indeed.

Most pyrotechnic reactions produce smoke that can play dual roles, both scoundrel and saint. As scoundrel, smoke can obscure the desired visual reaction thus rendering it less effective. Examples cited are color flame formulations (tracers, aerial stars, flares, etc). Mixtures of this type usually employ high oxidizer contents and/or metallic fuels that increase the combustion temperature which will reduce the quantity and density of the unwanted byproduct. The less the smoke, the more translucent the color.

On the other hand, smoke has many useful applications and compositions designed to *increase* smoke production are being continually sought and applied. Examples include but are not limited to; controlling or repelling insects and rodents, fungicides, biological applications, military and paramilitary roles, signaling and survival, troop, agency and employee training, movie and theatrical effects and rocket or munition tracking.

There are many useful material candidates for good smoke production. As stated, the term "smoke" refers to the suspension of fine solid particles in air. With this in mind, the candidate material must be combusted thus producing gasses and by-product solids which are dispensed into the air forming the desired quantity, density and color of smoke. Again, this is accomplished in a number of ways;

Generation through:

1) Combustion
2) Incomplete combustion
3) Sublimation / volitilization
4) Combined reaction(s)

Candidate materials from vast resources must be chosen carefully according to the desired effect in the reaction. This reaction would be one of both gas and solids yielding in volume at a combustion temperature low enough to get the job done without consuming much of the by-product solids that would otherwise be viewed as smoke.

Gas production formed through combustion of a fuel is a necessary by-product playing a dual role in smoke generation. By-product gasses form the **means** by which vaporized solid particles are dispensed to cooler air from a heated reaction zone condensing into smoke. The **volume** and/or density of smoke depends on the fuels combusted, the **rate** at which combustion and subsequent gas production takes place and the quantity of **moisture** (humidity) present in the air.

Heat of reaction is also very important in smoke generation where high combustion temperatures consume fuels more efficiently thus feeding on the vaporized material(s) to reduce their numbers. It is therefore important to keep the reaction temperature as low as possible yet adequate to reduce the fuel(s) to a gaseous state. Typical combustion temperatures for smoke compositions will range from approximately 400° F (color smoke) to 1200° F (chlorides).

Candidate material(s) chosen for:

1) Gas production (vaporized material)
2) Solid particle formation
3) Solid and vapor particle condensation

Combustion of a composition designed to create smoke would include a combination of one or more of the following candidate materials; fuel, heat and flame suppressors, oxidizer(s), organic dyes and chlorinated hydrocarbons. These combinations provide both smoke (solid particle formation) and gasses which provide the pressure needed to dispense vaporized materials rapidly from the heated reaction zone.

The events that lead to gas production and smoke generation occur in a heated reaction zone where combustion of a suitable fuel and oxidizer **vaporize** volatile ingredients. In the case of color smoke, a low heat reaction is required to sublime or vaporize an organic dye which is carried away from the reaction zone with gasses where it is cooled, attracts moisture in the air and condenses once again into micronized solid dye particles we view as color smoke. A heat and flame suppressor is added to color smoke formulations in order to keep the reaction at a low temperature to protect the vaporized dye from decomposing thus ensuring good color and quality. The <u>melting point</u> of the dye must be <u>lower</u> than it's decomposition point. The larger this spread, the better the dye will work for color smoke. This same type of (vaporizing) reaction also applies to sulfur, ammonium chloride and a few aromatic hydrocarbons.

The reaction creating white smoke is obtained, among others, by the formation of chlorides from a heated compound of zinc and a chlorinated organic hydrocarbon or a compound of phosphorous which also releases byproduct gasses with oxides. Both mixtures strongly attract moisture in the air to form the solid particles we view as white smoke. Sunny days and humid atmospheres will enhance both color and white smoke production. A caution when using phosphorous; it produces toxic acidic smoke - phosphoric acid.

CHOOSING CHEMICAL CANDIDATES

Combusted components used in smoke production, as with any pyrotechnic reaction, create a range of byproduct gasses and ash which may possibly be harmful to health and environment, it is important to choose formulations employing components that will favor standards and pose a minimal harmful effect on both user and environment. Included in the list of materials best avoided are (but not limited to); carcinogenic compounds and those issuing poisonous or acidic fumes with smoke. These should be avoided for obvious reasons.

Pyrotechnic smoke generation is the heat reduction of fuel(s) and a volatilizing agent. The choice of materials should be taken carefully in an effort to reduce or eliminate irritating or poisonous byproducts or combinations that render the composition sensitive to moisture, friction or impact. Mixtures should be stable under a wide variety of physical and mechanical storage conditions. Generally speaking, smoke production, although useful in many applications, is unwholesome to both health and environment. We do not endorse improper use of or lay claim that components and combinations studied herein are of a safe nature to construct, use or store. Any experiments with established compositions and modified or new formulations should enlist steps to calculate local health and environmental impact and reduce them accordingly to a satisfactory level. Smoke generation should always be done in well ventilated areas free of combustible materials.

NOTABLE CAUTIONS

A) **Combustion of phosphorous compounds;** Phosphorous (red or white) is easily ignited and burns producing acidic oxides which attract moisture to form dense white smoke irritating to skin, eyes and respiratory system. Use only in well ventilated areas and avoid inhaling smoke. Phosphorous compounds can be hygroscopic, sensitive (especially so with <u>any</u> oxidizer) and unstable accordingly. However, new formulations combining red phosphorous and a rubber binder are currently being tested and used.
Notation; *The Space Shuttle generates millions of cubic feet of toxic, acidic smoke with every launch. Environmentally speaking, is the use of small tactical or entertaining smoke devices actually a befitting problem?*

B) **Sublimation of sulfur;** High percentages of sulfur in smoke compositions generate toxic sulfur dioxide gas (SO_2) highly irritating to respiratory system and eyes. Such formulations are used extensively for rodent control and insecticide / fungicide treatment.

C) **Formulation of zinc chloride (HC smoke);** Reaction between zinc or a zinc derivative and a chlorinated organic compound (such as hexachloroethane) produces zinc chloride vapor ($ZnCL_2$) which can cause nausea and headaches with prolonged exposure. HC smoke compositions are extremely hard to ignite without a hot prime and compositions employing pyrophoric metallic zinc are sensitive to moisture and subject to spontaneous combustion if not protected properly in storage. This type of smoke (tactical, used extensively by the military and others) is irritating to the skin, eyes and respiratory system and should be used in well ventilated areas. Avoid inhaling smoke.

D) **Carcinogenic or toxic dyes;** Candidate dyes for color smoke production should be chosen carefully in an effort to reduce those that are highly toxic or carcinogenic (cancer causing) wherever possible. There are many organic dyes that fit the candidate group (see color smoke section) but are limited to those that have a lower melting point than their decomposition point. The larger the temperature difference between the two, the better the dye will work for smoke production. As with any smoke, avoid inhaling and use in a well ventilated area.
Notation; *One of the most popular dyes for color smoke (canary yellow) is Auramine which is considered carcinogenic.*

E) **Environmental factors;** In addition to the cautions listed above, smoke components must also be chosen for environmental stability. The compositions and devices made using them must be shielded from the harmful effects of moisture (including humidity) and the adverse effects that changing seasons bring during prolonged storage. This would include storing in sealed plastic bags or cartons in a cool, dry place.

LEAST HAZARDOUS SMOKE

There are many applications that require a non-toxic / reduced risk smoke where breathing of it would be unavoidable, indeed, intentional. Such applications would include indoor stage & theatrical effects and as a tactical training aid for military and professional response teams.

Smoke screens designed for such applications are not pyrotechnically generated but instead rely on the volatilization of non-petroleum oils or oil solutions. These would include mineral oils or glycerine solutions that are injected into a heated coil such as with a propane heated fogger or the muffler of an internal combustion engine. The "fogs" generated from these solutions are far less likely to create a health hazard to skin and lungs when breathed.

CHEMICAL CANDIDATES & APPLICATIONS

There are dozens of chemical candidates that may be used in combinations to create pyrotechnic and non-pyrotechnic smoke screens. The chart to follow depicts many of these agents along with their particular function.

APPLICATION LEGEND

A) Oxidizer	**B)** Fuel	**C)** Smoke production
D) Gas production	**E)** Heat production	**F)** Heat suppression
G) Stabilizer	**H)** Sublime	**I)** Combust
J) Volatilize		

CHEMICAL CANDIDATES FOR SMOKE GENERATION AND FUNCTION

	A	B	C	D	E	F	G	H	I	J
Aluminum, Al		X	X	X	X				X	
Ammonium chloride, NH4Cl			X	X		X		X		
Ammonium oxalate, (NH4)2C2O4H2O			X	X		X			X	
Anthracene, C14H10		X	X	X				X	X	
Antimony sulfide, Sb2S3		X	X	X					X	
Asphaltum, (hydrocarbon) / Binder		X	X	X				X	X	
Calcium carbonate, CaCO3				X		X	X		X	
Calcium silicide, CaSi2		X	X	X					X	
Cellulose acetate ** solution Polymer / Thermoplastic / Binder		X		X					X	
Charcoal / carbon, C		X		X					X	
Corn meal		X		X					X	
Dextrine ** C6H10O5 / Binder		X		X					X	
Dextrose, C6H12O6		X	X	X					X	X
Glycerine, solution, C3H8O3			X	X				X		
Hexachloroethane, C2Cl6	X	X	X	X	X				X	
Hexamine, (CH2)6N4		X		X					X	
Lactose, C12H22O11H2O		X	X	X				X	X	
Magnesium, Mg		X	X	X	X				X	

CHEMICAL CANDIDATES FOR SMOKE GENERATION AND FUNCTION

	A	B	C	D	E	F	G	H	I	J
Magnesium carbonate * MgCO3				X		X	X		X	
Magnesium oxide, MgO				X		X	X		X	
Mineral oil, solution			X	X				X		
Naphthalene, C10H8		X	X	X				X	X	
Organic dyes			X					X		X
Paraffin ** C26H54 / Binder		X		X		X	X			X
Phosphorous, red amorphous, P		X	X	X					X	
Polyvinylchloride ** (PVC), (CH2=CHCl)n / Binder		X	X	X					X	
Potassium chlorate, KClO3	X			X	X					X
Potassium nitrate, KNO3	X			X	X					X
Potassium perchlorate, KClO4	X			X	X					X
Red gum, accaroides		X		X					X	
Sodium bicarbonate, NaHCO3				X		X	X		X	
Sodium nitrate, NaNO3	X			X	X					X
Starch ** C6H10O5 / Binder		X		X					X	
Stearic acid * C18H36O2		X		X			X			X
Sucrose, C12H22O11		X	X	X					X	X
Sulfur, flour, S		X	X	X				X	X	
Wheat flour		X		X					X	
Wood cellulose, (C6H10O5)n		X		X					X	
Zinc powder, Zn		X	X	X					X	
Zinc oxide, ZnO		X	X	X		X	X		X	

* Also used to reduce sensitivity

** Also used as a binder, lubricator and/or moisture preventative

Sublime; To convert a solid substance by heat into a vapor and upon cooling, condense back into solid form (such as smoke particle formation). [a]The higher the humidity, the higher the density of the "fog".

Volatilize; To convert from a solid form or substance to a vapor or gas. See notation [a] above.

FACTORS GOVERNING SMOKE PRODUCTION

To produce consistent desirable results, factors governing performance must be held constant from batch to batch in order to obtain reproducible pyrotechnic behavior and end result. The primary variables are as follows;

1) **Chemical constitution;** The reaction between two or more chemical or metallic elements determines final demise and therefore, application. A chemical reaction consists of the combination and structural movement of atoms to produce a new species or structure. Fundamentally, the atom is the foundation of all matter consisting of a nucleus of neutral charged neutrons, positive charged protons and negative charged electron particles. These elements are combined to form compounds. Pyrotechnic chemical or elemental reactivity is primarily determined by the tendency of each element to loose or gain electron balance in the reaction, such as the heated exchange of various chemical, elements in a change of reaction product(s) (for this study, heat and smoke production). The process of reaction products in smoke generation compounds is thus heat, decomposition, gas evolution, element volatilization or sublimation, condensation for solid particle formation (new structure) and ash or slag.

2) **Moisture content;** Of particular concern is the affect that moisture has on the chemical composition itself. Moisture provides the "link" that may allow one element to prematurely react with another resulting in poor, inconsistent results, decomposition and possible spontaneous combustion if enough decomposition heat is generated. Compositions containing metals (especially noted are zinc and magnesium) or chemicals that react with moisture are of particular concern and steps must be taken in construction to safeguard the device from it.

   Compositions that require moistening for processing should employ wetting agents that can be easily and adequately extracted (or evaporated) from the final product quickly. Compositions that are moisture sensitive should employ binders that are not water solvable - indeed, alcohol or solvent soluble binders are best used here.

   The best procedure is one that A) avoids using hygroscopic materials or B) treatment to moisture-proof the exposed surface(s) and C) by final sealing in wax, lacquer or vinyl solution or storage in plastic bags or containers with a silica gel packet to absorb moisture keeping it from the composition.

3) **Particle size;** A general principle of pyrotechnic propagation is "the finer the particle size, the more reactive the composition". This is explained by the intimacy of the components of the composition when mixed. The finer their particle size, the more homogenous the mixture resulting in highly reactive compositions. This of course depending on their chemical constitution, intended function and design.

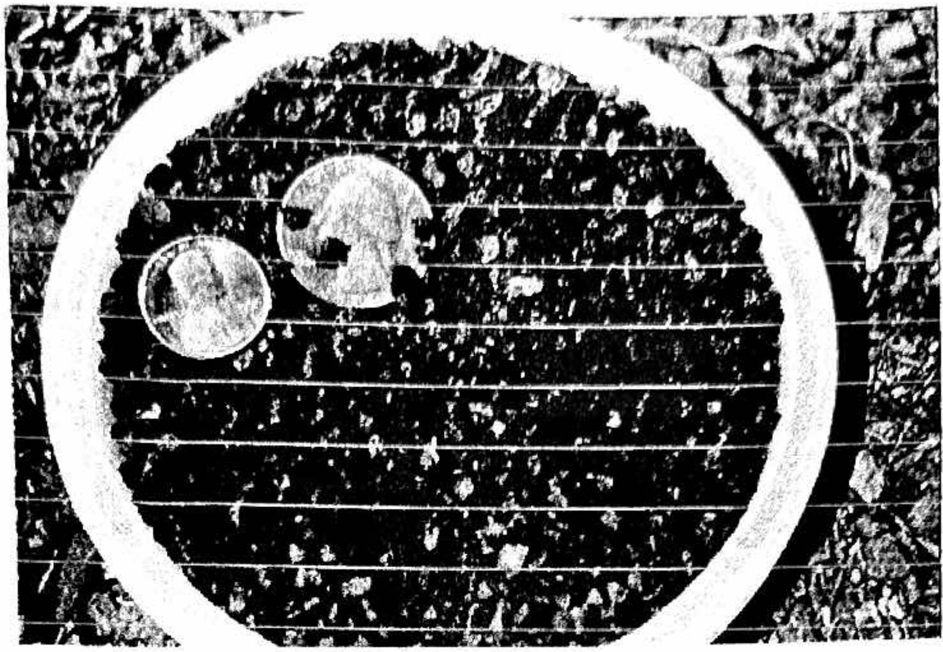
   Propagation also depends on particle size of the *composition* itself. Often, the combustion rate of the composition can be increased by increasing the surface area exposed to burn at one time. This can be accomplished by granulating the composition using a binder and raking the moist "dough" across a screen. The greater the surface area exposed to burn, the faster the combustion rate of the composition granule to granule.

These individual granules when combined supply a much larger surface area than that of a fine powder and when the composition is designed to produce smoke, the volume and density of the smoke increases as well and the burn *duration* decreases.

In use with smoke compositions, particle size determines many criteria for proper smoke production. The mixture must be blended to a well homogenized state which is best achieved with finely powdered ingredients. Homogeneity will increase as the component particle size decreases. Therefore, individually, the components are reduced to a fine powder before blending. However, smoke compositions employ a wide variety of candidate materials, each for its own properties or effect and they may be intentionally left in a granular state in an effort to further control the combustion rate and/or provide room for ash expansion as the composition combusts. For the most part, oxidizers, color dyes and most fuel ingredients are finely powdered (passing 150 mesh) for good processability (see sections on combustion, burn rates, surface of burn, consolidation, etc.). Bear in mind that ingredient segregation in storage or shipping will be more evident in compositions in the powdered state employing ingredients of varying particle size(s). If a larger granulation is required for one reason or another, it is better to granulate the *mixed composition* rather than employing ingredients of varying granulations (see sections on controlling burn rates and/or effects of component particle size, etc.).

4) **Consolidation;** Loading pressure plays a key role in the operation and subsequent production of smoke. Most smoke compositions depend on loose or porous grain formation to allow unrestricted passage of subliming product and gas through the developing ash. If this passage is blocked, (such as with a dense degree of confinement), the resulting smoke particle formation will be reduced according to the degree of obstruction. This is especially evident in color smoke production as the vaporized dye molecules attach themselves to developing ash if it is not porous enough to allow reasonable escape. Exceptions here would include sulfur / nitrate compositions, chlorides, insecticidal and others employed in dense pellet formation or candles. The combustion configuration of these types is a layer to layer "oscillation" burn where smoke formation does not particularly depend on condensation but rather sublimation. Such devices usually have low ash or slag development because of lower organic fuel(s) content and / or higher combustion temperatures.

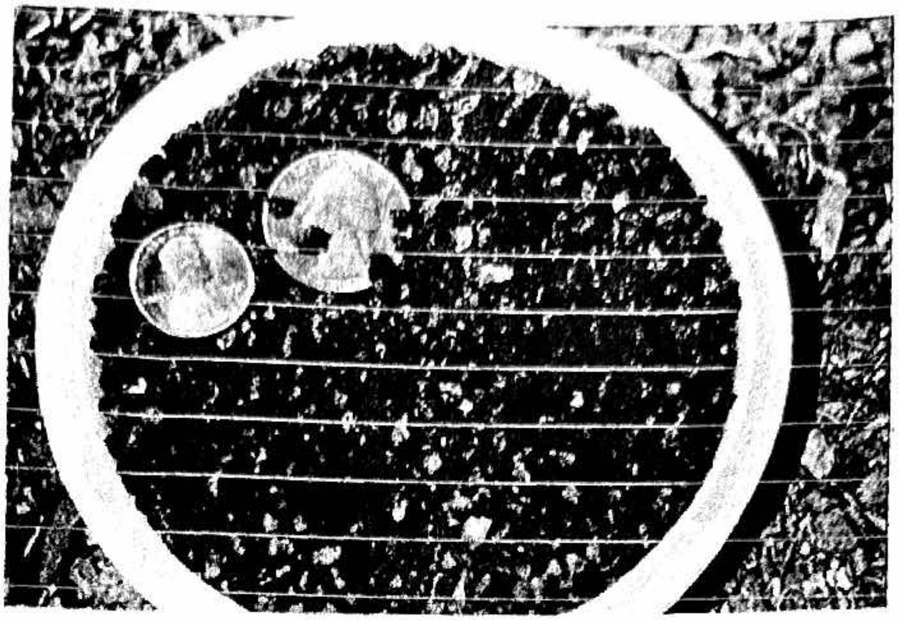
5) **Reaction surface area;** Surface area is critical in determining reactivity and smoke volume produced. Hand in hand with other criteria mentioned, smoke production is also controlled by the surface area exposed to burn (reaction surface area) where the desired heat yield and constant combustion rate is mandatory in proper smoke particle formation. Efforts to control output must include the controlled area of reaction. This is accomplished by; A) Composition granulation, B) Consolidation to limit exposed reaction surface, C) Grain formation - solid or cored, D) Containment dimension - controlling grain diameter, length and core, E) Combinations according to type of composition and the volume and density of smoke per the application.



6) **Combustion rate;** The rate at which a contained composition burns is termed in linear units of measure. For most pyrotechnic devices, fast reaction rates are measured in **meters** per second and slow rates in **centimeters** per second. Smoke device reaction rates are also measured in **seconds** with smoke production in **cubic feet**. Combustion rates are varied by altering ingredients and other criteria mentioned in this chapter. Be aware that loading pressure (consolidation) also plays a key role in combustion rate. General pyrotechnic reaction rates can be significantly altered by loading pressure (such as with solid rocket motors) where an increase in grain formation pressure leads to an increase in burn rate (measure in grams per second). This increase in combustion rate increases as the chamber pressure increases. The higher the chamber pressure, the faster the combustion rate of the propellant. Generally, compositions having highest flame temperatures ("high energy mixtures") produced by larger percentages of oxidizer(s) and / or metals also represent the faster combustion rates. As smoke compositions usually require low heat combustion and operate under low internal pressures, they are termed as "low energy" mixtures having controlled rates of reaction for both temperatures generated and smoke volume produced per device in any given time.

7) **Heat of reaction;** Expressed in units of calories per gram where one calorie of heat is required to raise the temperature of media (such as H_2O) by one degree (celcius). With this, we find the temperature increase of a measured amount of media resulting from the heat release of a measured amount of composition being converted into calories of heat from the reaction.

Reaction heat from pyrotechnic smoke production is very important. Unlike high energy mixtures, best smoke production is a product of combustion inefficiency obtained by a controlled low heat combustion or incomplete combustion of ingredients with an absence of visible flame which would reduce smoke particle formation by decomposing sublimed or volatilized vapors.



6) **Combustion rate;** The rate at which a contained composition burns is termed in linear units of measure. For most pyrotechnic devices, fast reaction rates are measured in **meters** per second and slow rates in **centimeters** per second. Smoke device reaction rates are also measured in **seconds** with smoke production in **cubic feet**. Combustion rates are varied by altering ingredients and other criteria mentioned in this chapter. Be aware that loading pressure (consolidation) also plays a key role in combustion rate. General pyrotechnic reaction rates can be significantly altered by loading pressure (such as with solid rocket motors) where an increase in grain formation pressure leads to an increase in burn rate (measure in grams per second). This increase in combustion rate increases as the chamber pressure increases. The higher the chamber pressure, the faster the combustion rate of the propellant. Generally, compositions having highest flame temperatures ("high energy mixtures") produced by larger percentages of oxidizer(s) and / or metals also represent the faster combustion rates. As smoke compositions usually require low heat combustion and operate under low internal pressures, they are termed as "low energy" mixtures having controlled rates of reaction for both temperatures generated and smoke volume produced per device in any given time.

7) **Heat of reaction;** Expressed in units of calories per gram where one calorie of heat is required to raise the temperature of media (such as H_2O) by one degree (celcius). With this, we find the temperature increase of a measured amount of media resulting from the heat release of a measured amount of composition being converted into calories of heat from the reaction.

Reaction heat from pyrotechnic smoke production is **very** important. Unlike high energy mixtures, best smoke production is a product of combustion inefficiency obtained by a controlled low heat combustion or incomplete combustion of ingredients with an absence of visible flame which would reduce smoke particle formation by decomposing sublimed or volatilized vapors.

Reaction heat is best controlled by the ratio of oxidizer to fuel(s), the type of oxidizer used and the percentage used in the formulation. The larger the oxidizer percentage, the faster the combustion rate accompanied by a likewise increase in combustion temperature. In an effort to control this, smoke compositions often employ the use of a low reaction heat oxidizer such as potassium chlorate and supply a "cooling zone" within the casing to allow vaporized material(s) to cool prior to contact with air outside the reaction zone where moisture changes it into solid particles we view as smoke.

8) **Confinement;** The internal pressures generated and the material(s) used to confine (container controlling grain geometry) will determine much of the performance and overall smoke production. Containers that are low in thermal conductivity (such as cardboard) will absorb excess reaction heat rather than transferring it to the un-reacted grain or mass. This helps keep heat radiation down and improves vapor cooling and condensation. The same composition in a metallic container will combust at a faster rate due to the increase of heat conducted by means of the container to the grain "pre-heating" the composition ahead of the reaction zone thus speeding the burn rate. Metallic fuel in the composition itself has the same effect.

The degree of confinement refers to the internal pressure created by the rapid release of reaction gasses and heat. This pressure is regulated by the size of the vent or choke in the device. If this release is restricted by smaller vent(s), an increase in pressure will occur with a likewise increase in heat and combustion rate. A faster combustion rate increases the volume of smoke produced but the increase in heat generally *decreases* the density of the smoke (depending on the type of smoke being produced). Here, worst case scenario would be compositions employing color dyes or other materials that are decomposed by heat thus reducing the color and/or density of smoke particle formation. Keeping the reaction heat down by employing coolants in the composition and/or supplying a cooling zone in the design markedly increases smoke volume *and* density. A test or two will determine the proper balance between vent size and grain diameter for optimum results.

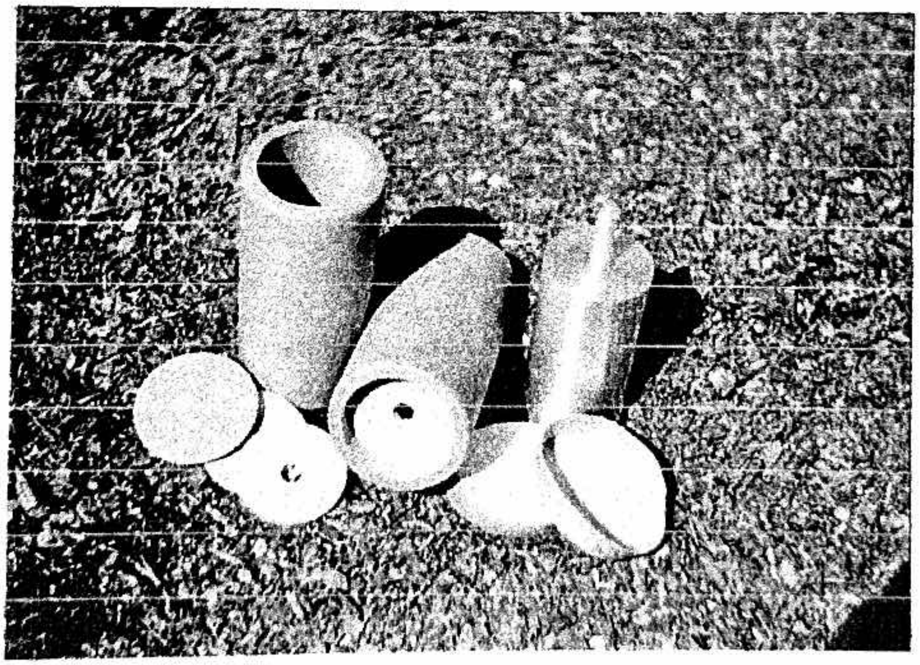
9) **Volume of byproduct gas(es);** Gaseous combustion byproducts are essential in dispersing vaporized smoke component particles. These gasses (mainly CO & CO_2) are the "stream" that transfers sublimed or volatilized vapors from the reaction zone to be cooled. These non-flammable gasses also displace oxygen within the reaction and cooling zones to eliminate possible flaming that would destroy optimum smoke production. The amount of gaseous product markedly effects the dispersion of these vapors. Generally speaking, all components of smoke mixtures, whether exothermic or endothermic in nature, produce combustion gasses aside from smoke production within the reaction. Candidate materials should be chosen for their particular role in the combustion process which provide both heat suppression and stabilization in addition to their gaseous byproducts. Examples are $CaCO_3$, $MgCO_3$ and $NaHCO_3$. Best smoke production occurs when copious amounts of these gasses are produced with vaporized smoke producing agents. Organic and/or sulfur compounds generally provide the best levels of "naturally" produced gasses. "Gassless" compositions such as delay mixtures would employ a minimal percentage of such materials.

10) **Environmental effects**; Climate conditions that affect stability and storage conditions also affect proper smoke production in use. As stated, moisture (including high humidity) as well as heat can destroy or reduce the effectiveness of unprotected pyrotechnic compounds and devices made from them, yet these same conditions can enhance the desired effect in use by increasing the density of the smoke produced.

Reaction products that strongly attract moisture and condense to form the solid particles we view as smoke are enhanced in moist, humid climates because the condensation process of vaporized materials is accelerated by rapid cooling in moist air. Smoke produced from large quantities of sulfur may be the exception to this process. The process to create smoke from sulfur compositions is more of a sublimation than condensation and therefore is not adversely affected by moisture in the air.

Color smoke production also uses condensation to convert volatilized dye vapors back into solid color particles in air, however, sufficient light plays a strong role in perceiving the true color as intended as well. Dull, cloudy or shaded areas or breezy conditions all degrade rich color and should be taken into consideration during testing and use.

CONTAINERS & CONSTRUCTION



We have previously discussed factors governing smoke production and application. Bearing these in mind, we can refine construction procedures adequate for each type of composition used. Smoke devices can be constructed in a variety of sizes, shapes, burn durations and smoke color. Construction of the container and/or grain shape should correspond directly with the type of composition used, the combustion temperature and total burn duration as per the application.

Devices designed to produce smoke also produce heat. The container must be designed to contain the heat and superheated gasses in an effort to control burn through and possible range fires during use. Heavy walls treated with a fire retardant and/or refractory agent should therefore be considered mandatory when combustible casing materials are used. In addition, because of the hygroscopicity of most smoke compositions, final case treatment to retard moisture is also necessary to insure optimum performance. There are many moisture preventatives in the form of waxes or lacquers that are available for use.

BURN TEST RESULTS - EXAMINATION PROCEDURE

At the end of each burn, the casing was immediately examined for evidence of heat and gas erosion to the inner and exterior surfaces of the casing. Results are listed per test.

Test 1

Composition	Color smoke dye / organic fuel(s)
Est. Burn Temp	400-450°C (752-842°F)
Burn Duration	80 seconds
Container	Cardboard, spiral wound kraft 2.50" OD X 5.00" Long X .25" Wall
Retardant	Firefox liquid fire retardant, container dip saturated

Results;

Container was warm but not uncomfortable to the touch. No evidence of heat damage was found on the outside surface. Casing was cut lengthwise with band saw, ash examined and removed. Further examination showed that the inner casing wall *above* the ash (cooling zone) was blackened by the heat but not charred whereas the surface contacting the ash (reaction zone) was charred slightly - burned on the surface only.

The same test was conducted exactly as listed with one exception: **No** fire retardant was used. The difference was as noted; Casing was hot after burn instead of warm and the inner reaction zone surface had been charred into additional layers of paper (approximately twice as much burn erosion). No visible sign of exterior surface heat damage.

Test 2

Composition	HC type, white
Est Burn Temp	900-1000° C (1652-1832° F)
Burn Duration	75 seconds
Container	Cardboard, spiral wound kraft 2.50" OD X 5.00" Long X .25" Wall
Retardant	Firefox liquid fire retardant, container dip saturated

Results;

The container was too hot to be handled comfortably yet had no visible sign of exterior heat damage. Upon cutting open, ash was removed and casing examined for damage. Deterioration from heat was much higher than test 1. Surface charring was evident in cooling zone (burned into 2+ layers of paper) while the reaction zone posted heat damage of approximately .065" (1/16") into the casing wall.

Performing the test **without** retardant, the reaction zone showed heat damage of approximately 50% of wall thickness with evidence of slight heat browning on exterior surface. Casing was brittle and easily crushed by hand. Alternately, additional tests were performed;

A) Coating the reaction zone surface (still wet from the liquid retardant) with a thin layer of magnesium oxide (MgO). Results were only slightly better than test 2 (fire retardant only) in that measured effects of heat were minimally in favor of using MgO as an additional refractory coating.

B) Applying a layer of carbon cloth to the inside of the casing previously treated with fire retardant liquid (while still wet) which acts as an adhesive to hold it in place. The vent may also be similarly coated. This combination was by far the most effective in controlling heat damage. The carbon cloth acts as an insulator between the heat and the fire retardant impregnated paper thus practically eliminating any charring.

Firefox Enterprises Inc. supplies carbon cloth in many widths. It is inexpensive and easily cut with scissors to any shape required.

ADDITIONAL COMMENTS

The above test results are given as reference for better understanding between variables of low and high combustion temps and the subsequent heat damage. It is the author's opinion that smoke devices of similar burn duration using paper casings employ similar means to reduce heat erosion. The high combustion temperatures of HC compositions should employ casings with wall thickness of 1/4" additionally treated with a fire retardant material to help ensure against possible spot fires when used in the field. Likewise, the vent(s) and end-wall (case bottom) must also employ similar measures such as those mentioned in "B" above.

In summation, remember that even though smoke producing compositions / devices are designed to function with an absence of flame, they *do* produce intense reaction heat damaging to not only the container itself, but possibly the environment in which it is used should the container fail to properly insulate and repress heat and ash buildup. High combustion temperatures and long burn durations require the best container designs possible.

EFFECTS OF COMPONENT PARTICLE SIZE COMPOSITION GRANULATION

In reference to part 3 (particle size) pages 14-18 of "Factors Governing Smoke Production", we will review the following points;

A) Particle size versus composition reactivity
B) Ingredient homogeneity versus segregation
C) Composition granulation versus combustion rate

There are many variables to consider when designing formulations and choosing components for pyrotechnic devices. Smoke compositions generally require fine component particle sizes to achieve complete homogeneity, providing smooth combustion and volumes of dense smoke. The lack of larger component particles within the composition (intentionally added to control combustion rate or reduce density) would decrease possible segregation in shipping and storage while increasing un-molded reactivity but would possibly pose an additional problem of molded composition density which affects smoke particle formation during ash development under combustion. Vaporized material(s) **must** be allowed to escape the confines of ash freely to cool and exit the case with byproduct gasses to form the desired smoke cloud in the moist air. Once powdered, densely molded compositions produce a more solidly (dense) formed ash column that obstructs free vapor escape. The answer is not variant component particles or compressed powder columns but a working combination of molding the composition within the case supplying a center core and / or granulating the composition. Both provide an escape route for the vaporized materials but they vary in combustion rate. A solid formed grain using *powdered* composition with a center core will combust more slowly than a pressed *granulated* composition. The latter having the larger surface area and therefore the faster combustion rate. A combination of the two will yield the highest combustion rates and therefore larger volumes of smoke per second of burn.

The granulating process takes place following full homogeneity of mixed component materials with a small percentage (2-4%) of a compatible binder. Care must be taken during the process to insure against accidental ignition. Whereas strong oxidizers are present (chlorates of particular concern) caution cannot be overstated. Thorough remote mechanical mixing or milling of ingredients (without oxidizer) followed by homogenous mixing with the oxidizer will yield the best results with a minimum of personal risk. As with *any* pyrotechnic composition, the process of granulation and drying of smoke compositions is undertaken with caution using non-sparking equipment and processing materials (brass or aluminum screens, containers, mixing equipment, drying trays, etc.) in an approved unobstructed area.

GRANULATING PROCEDURE

Once blended, the composition is moistened with the appropriate binder solution to a dough-like mass and scraped across a coarse mesh screen of approximately 6 to 10 mesh over a shallow tray covered with a sheet of paper. The trays can then be dried in the hot sun or placed within a rack located in a drying room or "box" protected from moisture, high humidity, open flame or intense heat in excess of 150° F that may ignite the material.

Once dry, the grains can be sieved or further reduced to satisfy specific grain size requirements. Being of well mixed composition, these grains are not subject to segregation in shipping or storage and provide better surface area for combustion while retaining individuality, each retaining its own surface area even after pressing into particular shapes. This individuality provides "channels" between each grain thus providing a porous ash to speed vaporized material(s) release from the reaction zone. This creates rich smoke color and dense clouds.

COLOR DYE PROCESSING NOTE

The handling and use of dyes for color smoke production is a messy undertaking which is augmented by the addition of moisture. Steps to protect your hands, equipment and bench top must be taken in processing to insure against permanent staining. The use of disposable processing materials is highly recommended. However, once the mixed composition *is* granulated and dried, it is easier to use and less messy due to the reduction of fine dusts that can be airborne and carried to other surfaces to stain.

GRANULATION EFFECTS ON COMBUSTION RATE

First, lets revisit pages 14 section 3 (particle size), page 15 section 5 (reaction surface area) and page 16 section 6 (combustion rate). Essentially, the information in part relates to combustion rates as controlled through the surface area of burn whereas the overall surface area of each granule determines its reactivity. Burn rates **increase** as the surface area exposed to burn increases. A good example of this is small arms sporting "Black Powder". The *smaller* the grain size, the faster the burn rate due to their greater surface area (over that of larger grains) that are exposed to burn at a given time (per gram) which is faster than larger grains of the same composition and test sample weight. Black powder becomes explosive because of confined pressure of heated gasses leading progressively to accelerated burning and even higher heat and gas pressure buildup eventually leading to explosion - all in a millisecond. Because of low pressure through vented casings, conventional smoke devices are not subject to explosive pressure buildup but the reaction of granulated product is essentially the same as the black powder burn test at a scaled down rate.

To test this point we constructed three devices similar in design to the diagram on page 18. All three devices contained the same composition but different granulations.

Test 1

Device grain description	Core molded, light hand pressure only
Composition	Color smoke dye / organic fuel(s)
Composition granulation	Powder
Oxidizer content	25% by weight ($KClO_3$)
Composition weight	3.0 oz (85.05 grams)
Estimated burn temperature	390° - 410° C

Burn duration *	140 seconds
Estimated smoke volume / sec	714 cubic ft (ft^3) / sec (fills an area 10' X 10' X 7' **per second**)
Total smoke volume	100,000 cubic feet (ft^3) light density

Comments; Color of smoke faded @ 87 seconds into burn and continued to further degrade in color to a dull grey / white @ 110 seconds through end of burn. Volume of smoke was consistent throughout the burn. The ash was solidly formed with very little porosity.

Test 2

Device grain description	Core molded, light hand pressure only
Composition	Color smoke dye / organic fuel(s) (same)
Composition granulation	12 mesh (.060 or approximately 1/16" diameter)
Oxidizer content	25% by weight ($KClO_3$)
Composition weight	3.0 oz (85.05 grams)
Estimated burn temperature	390° - 410° C
Burn duration *	97 seconds
Estimated smoke volume / sec	1031 ft^3 / sec (fills an area 10" X 10" X 10" **per second**)
Total smoke volume	100.000 ft^3 light density

Comments; Good rich color until approximately 93 seconds into burn then faded for remaining four seconds of burn. Smoke volume was consistent throughout burn. Porous ash column.

Test 3

Device grain dimensions	Core molded, light hand pressure only
Composition	Color smoke dye / organic fuel(s) (same)
Composition granulation	5 mesh (.159 or approximately 5/32" diameter)
Oxidizer content	25% by weight ($KClO_3$)
Composition weight	3.0 oz (85.05 grams)
Estimated burn temperature	390° - 410° C
Burn duration *	122 seconds
Estimated smoke volume / sec	820 ft^3 / sec (fills an area 10' X 10' X 8' **per second**)
Total smoke volume	100,000 ft^3 light density

Comments; Good color up to approximately 117 seconds gradually fading to grey / white at end of burn. Consistent smoke volume throughout burn. Porous ash column.

* = subject to slight variations according to loading pressure used

When using granulated compositions, it is not necessary or practical to screen and separate according to size for general use. We have done it merely to show the difference in smoke volume produced per second according to burn rates as governed by particular particle sizes. In using compositions of various particle sizes, with concern for a controlled burn duration, the length of burn itself can be adjusted by the quantity of composition used, the length of (or absence of) a center core, re-designing the geometry of the device itself to combust at more than one surface area or using compositions of varying oxidizer to fuel(s) loadings. All of these steps may be employed with granulated compositions without degrading the quality of the smoke.

FIGURING SMOKE VOLUME & DENSITY

The volume and density of smoke produced during the reaction can be expressed in terms of **particle concentration** (density) per gram of composition at a given burn rate. Whenever figuring smoke density, the following factors must be considered;

1) **Formation rate;** The rate at which vaporized smoke material(s) (expelled with byproduct gasses) or solid particles generated through incomplete combustion (such as black soot smoke compositions) are formed or released in air.

2) **Particles per unit of volume;** The quantity of solid smoke particles present within a specific volume area (particle concentration) at a given time.

3) **Concentration weight;** Represented by the rate of fall or displacement in a continuous motion of air as related to gravity, air current, heat and humidity.

For our tests, we have shown the volume of smoke (expressed in cubic ft - ft^3) generated each second during the reaction. The equations are expressed as follows;

Legend

G = Total ft^3 generated
D = Total burn duration / second
C = Total composition weight
FS = Cubic ft / second
CR = Consumption rate
PG = Smoke produced ft^3 / gram
RG = Burn rate ft^3 / gram

Smoke produced ft^3 / second

$$\begin{array}{c} FS \\ D\sqrt{G} \end{array}$$

Composition consumed grams / second

$$\begin{array}{c} CR \\ D\sqrt{C} \end{array}$$

Smoke produced ft^3 / gram

$$\begin{array}{c} PG \\ C\sqrt{G} \end{array}$$

Burn rate ft^3 / gram

$$\begin{array}{c} RG \\ C\sqrt{FS} \end{array}$$

These equations can be used to compare the operation and performance of various devices and compositions. . For example, if a thick, dense cloud is required for tactical operations or concealment, a device that is said to offer total smoke production of 120,000 ft^3 and a burn duration of three minutes is not necessarily better for the application than one that delivers 90,000 ft^3 in seventy seconds. The faster a stated quantity of smoke is produced, the more dense will be the obscuring cloud providing of course the composition and factors in both tests are equal. For this reason, military devices are of short duration , that is to say, they are designed to produce huge volumes of smoke in a short period of time thus producing a heavy, thick smoke cloud that remains close to the ground to effectively cover troop movement (additional information on military smoke devices will be covered later in the text).

Factors to consider when comparing commercial smoke devices;

1) Intended application
2) Total smoke production ft^3
3) Total composition weight
4) Total burn duration

In shopping for or designing smoke devices, knowing these factors and applying the equations, precise evaluation and custom design and operation can be calculated according to the application and desired effects.

FIGURING UNKNOWN SMOKE PRODUCTION / TOTAL FT^3

Calculating overall smoke production when it is unknown depends mainly on the users idea of density required relating to the application. When designing smoke devices, one must first have knowledge of intended use. For example, in use for determining design or air flow, (as in wind tunnel applications) or showing wind current, direction, etc., smoke should be a steady stream of long duration and can be of lower density such as using a long slender smoke "stick" or "candle". On the other hand, if the application calls for signaling or obscuring movement or location, the device should be designed with shorter burn durations and larger volumes of smoke such as that produced from tactical smoke device designs employing a center core for increased burn surface. This density or smoke particle concentration can be calculated in a number of ways assuming a particular application is mandatory. Of course, the easy way would be to ignite a device of particular composition weight within the confines of an enclosed area and calculate cubic feet generated by multiplying the length X width X height of the enclosed area. If the smoke cloud is thick enough according to application in mind, the total smoke volume in ft^3 per measured quantity of composition is now known and other calculations and changes may be made accordingly.

A practical way of measuring density is a simple device constructed of glass and an electric light. First, construct a glass box open at the bottom one foot square and mount a light socket with a low watt (25-60w) bulb outside the box at the back side. Now, using a photographic light meter, take a reading of the unobstructed light holding the meter to the front of the box and record the reading. Place a gram or two of smoke composition in the box and ignite it allowing the box to contain the smoke and record the burn duration. A second reading is now taken of the light intensity through the smoke, recorded and compared to the first reading. Several tests are conducted in this manner using various compositions and controlled quantities to be later equated and used to design devices befitting particular applications. Be sure to clean the glass between tests to obtain accurate readings. The best results are those tests using minimum composition quantities resulting in lowest light readings through the smoke.

Equations that can be used to calculate smoke volume and optical density (particle concentration) using the device previously discussed can be expressed as follows;

Legend

DV = Desired total volume smoke (ft^3) per device
LE = Intensity of measured light entering the box
LL = Intensity of measured light leaving the box (through the smoke)
TS = Thickness of smoke layer (curtain) in these tests, one ft (1.0')
QC = Quantity by weight of composition used to obtain desired optical density (OD) in cubic feet (ft^3)
OD = Desired optical density (% or coefficient)
MC = Mass of composition to produce total desired smoke volume (ft^3)

Testing the value of a tailored smoke producing composition

LE - LL = OD (coefficient desired) @ 1 ft^3
OD (%) = LE ÷ 100 X OD
MC = QC X DV
QC ÷ 1 ft^3 = MC ÷ DV

The equations express the desired volume and optical density in percentage. When using a light meter, the scale is 0 to 10 in measured incident and reflected light entering the meter. This scale can be left as whole numbers, converted into fractions or used as percentage figures to obtain LE and LL thus supplying the "coefficient" figure in the equation. Using our device, the first step is to obtain the desired OD. This ability of "hiding" or "darkening" (coefficient) is expressed here in percentage. Example; If LE = 10 and LL = 5 using .1 gram of composition (QC) and the hiding power (density) is adequate according to the intended application, the density coefficient is .5 or 50% per 1 ft^3 @ .1 gram (QC). The equation is based on adequate OD.

LE = 10
LL = 5
____
5 = 50% or .5 (density coefficient)

If an increase in density is required, the coefficient increases as LL decreases. Example;

LE = 10
LL = 3
____
7 = 70% expressed as .7 = 10 ÷ 100 X 7 (70%)

When designing devices to produce larger specific volumes of smoke (example 100,000 ft^3 or an area of approx 70' x 70' x 20') with a 70% coefficient obtained by the reaction of .1g composition within 1 ft^3 (where m = 1000) the resulting MC = .1g x 100m (or 10m total comp). Equated as;

$$QC \div 1\ ft^3 = (MC \div DV) \text{ or } 10m \div 100m = .1$$

Where OD = 70% @ 1 ft^3 (TS) the resulting device would create a smoke screen (with 70% hiding power per 1 ft curtain in thickness) or in theory, 1 ft wide x 10 ft high x 10,000 ft long (providing all factors stay in balance and particles do not fall or further scatter dimensionally). Remember, in theory, the device has a 70% density coefficient per **ft** of smoke in thickness and it generated 100,000 ft^3 total smoke in volume.

We express this figure of OD as example only in an effort to compare smoke production values. However, in reality, most smoke devices (using comparative methods) have OD values of **less** than 10% enabling them to advertise high smoke volume ft^3 because the optical density is based on a very thick smoke curtain to obtain an un-advertised degree of obscuring properties. As the thickness of smoke (TS) increases, the optical density (OD) decreases unless an increased quantity of composition is also used keeping it in balance and all other factors are in balance accordingly. Therefore, to find values of increased smoke volume production (at comparative OD coefficients) we express it as follows;

$$MC = QC \times DV$$

Resulting OD of the larger cloud would be similar (providing cubical dimension area increased at a proportional rate to that of test chamber) but would vary according to a dimensionally changing cloud formation and rate of movement in open air. Total composition (MC) must be increased proportionally to the total volume of smoke desired (DV) to produce similar OD coefficients in comparatively restricted dimensional enlargement.

In design, if the desired optical density can only be obtained from an unusually large quantity of composition tested, steps should be taken to check for adequate smoke particle formation by reviewing the factors involved and making adjustments accordingly or by changing to another composition formulation completely. As example, a good design starting point using the apparatus previously discussed can be written;

Intended application:	Emergency signaling or marking positions
Desired total smoke volume:	100,000 ft^3
Desired burn duration:	60 to 90 seconds
Test chamber:	1 ft^3
Test lamp:	Wattage required to register 10 on the meter without burying the needle
Desired optical density:	25 to 50%
Weight quantity of composition:	Adequate to produce desired optical density

NOTES ON TACTICAL MILITARY SMOKE DEVICES

Because of their unique construction and large volumes of smoke produced, military smoke grenades are in high demand when surplus stocks are available brining $30.00 to $40.00 each. They feature dependable ignition and their design produces huge volumes of richly color or white smoke in 60 to 90 second burn durations.

The primary design of the device is to generate large volumes of smoke that is heavy enough to stay lower to the ground rather than rising rapidly to dissipate. This dense particle formation produces a cloud formation capable of obscuring troop movement or for long distance signaling. It is accomplished by the use of 10-14 ozs of composition pressed with a thermite core for ignition ease and increased surface of burn. This high particle concentration mixes with moisture in the air and coagulates to form the dense cloud structure which is further enhanced in warm humid environments.

Comparative white smoke devices using formulations containing NH_4Cl and/or C_2Cl_6 (as well as color smoke) can be easily and inexpensively produced using information contained in this text. The container must be treated to retard moisture and must have a wall thickness adequate to insulate against possible burn through according to the design and burn duration. Treated paper casings should be approximately .25 to .35" in thickness per 60 second burn and increase in thickness as the burn duration increases.

CONTROLLING BURN RATE, SMOKE VOLUME AND FLAMING THROUGH DESIGN

As we have only briefly discussed various points of these subjects, we will now study them in greater detail as they are of particular concern in productive smoke devices.

Burn rates are controlled mainly by the oxidizer percentage and surface area of burn. Increasing the oxidizer percentage in the composition in an attempt to increase combustion for greater volumes of smoke will most likely do more harm than good. As oxidizer ratios increase, so does the heat of combustion and likewise, the possibility of flaming which destroys smoke particle formation. For this reason, oxidizers of low ignition and reaction temperatures are employed. Where it can be used, the obvious candidate here is potassium chlorate ($KclO_3$) which provides low ignition points and reaction heat adequate to vaporize smoke agents with a minimum of its percentage. It decomposes well below 400° C forming KCl, oxygen and other gasses such as CO, CO_2 and others according to the fuels and stabilizers used.

Oxidizer ratios by weight per classification

1) Combustion	25-50% (up to 65% if C_2Cl_6 is sole oxidizer)
2) Incomplete combustion	45-55%
3) Sublimation / volatilization	22-32%
4) Combustion reactions	20-30%

When tailoring compositions to increase smoke production, granulating a workable composition or supplying a center core in the grain to increase surface of burn is best. This not only accelerates the burn rate by providing greater reaction surface for increased smoke particle formation, but also helps control flaming which occurs if the percentage of oxidizer is mistakenly too high thus creating excess heat. Supplying a "cooling zone" separate (above) from the reaction zone (burning surface) also aids in solid particle formation by allowing the vaporized particles to cool before exiting to mix with moisture in the outside air. The cooling zone, properly vented and minimally pressurized by ensuing gasses from the combustion process, displaces atmospheric oxygen thus keeping it from the reaction which in turn helps control burn rate, heat buildup and flaming to promote solid smoke particle formation for rich color and high density smoke clouds.

In cases where composition granulation is not practical (where addition of moisture may cause spontaneous reaction such as C_2Cl_6 / Zn mixtures with water soluble binders) various designs utilizing loosely placed powdered compositions can be employed with good success. An example here is a suitable container with compositions of adequate oxidizer ratio to ensure ignition and propagate without flaming in open air (see next section on composition testing). Upon loading, the container is then supplied with three to five 1/4" diameter holes evenly spaced on a spiral line starting in the center of the casing and toward each end. The device is then ignited through the center hole and combusts equally toward each end venting an increased volume of smoke as supplied by the greater surface area of burn (spirally in both directions from center) and multiple vents. Increasing the diameter and length of the container also increases smoke volume and burn duration and devices for particular applications are designed accordingly. Compositions that can be used in this manner include all four classifications listed on page 7 herein, providing they combust to produce smoke <u>in open air</u> *without* voluntary flaming.

Another design similar in construction to that on page 18 using a powdered composition sealed with a layer of prime composition thinned with lacquer to retard moisture and provide positive ignition. The procedure uses a ram with a tapered spindle to lightly compress (by hand) the composition forming a core within. A length of match or fuse is placed in the core and a thinned slurry of prime composition in NC lacquer or cellulose acetate solution is added to "cement" the fuse in place and coat the exposed surface of the smoke grain to seal it from moisture and retain the formed grain shape. Upon ignition, the prime ignites all coated surfaces for volumes of smoke aided by a mildly compressed smoke composition providing porous ash development to aid the escape of vaporized smoke agents. Again, compositions from all four classifications can be used here with good success.

TESTING FOR PROPAGATION, SMOKE & ASH DEVELOPMENT

When testing a tailored composition to determine applicability, an easy method (without the expense and time of constructing a complete device) is to test burn the composition in open air to observe propagation, signs of visible flame, smoke production, and resulting ash. Pre-testing compositions in this manner will quickly supply information accurate enough to warrant further tests of particular designs. Here, the results are analyzed and the formulation adjusted where necessary for optimum performance with final testing done as a completed device. It should be noted that compositions of higher reaction temps (800° C+) are likely to produce visible flame in open air (the likelihood of which increases in breezy conditions) than those of lower reaction temps such as color smoke compositions and for this reason, the tests are only preliminary and unsatisfactory results should not be discarded and thus considered useless. Such compositions can often be adjusted for use here or other applications.

Factors to consider in preliminary tests;

A) Ease of ignition
B) Propagation: smouldering or flaming (reaction heat)
C) Smoke volume and depth of color
D) Duration of burn per ounce
E) Ash quantity and density (porosity)

PROCEDURE

One ounce of composition is placed within a shallow open tin or similar container of approximately 1 1/2" to 2" ID and 2" in depth, lightly pressed in by hand and fused with the appropriate ignition source. Upon ignition, the factors are observed, burn duration timed, ash weighed and results recorded (including smoke volume, color and density) for further evaluation.

A) **Ease of ignition;** The composition must ignite easily using a source appropriate to that of the classification used (page 7). Opposite examples cited are; for ease of ignition without hot priming (class 3) or for those difficult to ignite requiring hot "slags" or thermite (class 1) C_2Cl_6 / ZnO type mixtures.

B) **Propagation;** The composition should "smoulder" without flame at an even rate producing good smoke in volume. However, as noted, in open air the reaction can occasionally flame due to an excess of oxygen at reaction level which is absent in a confined reaction protected from atmospheric oxygen which is displaced by ensuing unreactive by-product gasses and smoke. Reliable compositions should combust smoothly and rapidly producing large volumes of smoke. If the reaction is unsatisfactorily slow, with absence of visible flame, increase the oxidizer content in small 1-2% increments until visible flame is apparent. If the flame can be extinguished by covering for a moment with the composition smouldering, and it does not burst immediately into flames once the cover is slowly removed, the oxidizer percentage is correct and the composition should be tested further in a completed device. Excessive oxidizer content increases oxygen in the reaction raising heat which causes flaming. As noted, this also applies to *atmospheric* oxygen entering the reaction zone. The percentage of oxidizer and the design of the device itself is adjusted in this respect.

C) **Smoke volume & depth of color;** Carefully constructed formulations will produce appropriate smoke properly contained with volume, burn duration and color quality controlled through device grain design and composition granulation. A problem often encountered with color smoke is poor color most often caused by a dense ash formation blocking much of the volatilized dye particles from proper exit. If a powdered composition is pre-tested and conforms to all necessary qualities including good color but fails to reproduce good color throughout burn in final device testing, the answer is **composition granulation** for single vent devices (page 18) or **loosely placed** compositions in containers with several vents on a spiral line around the outside of the casing.

Compositions producing white smoke are easily formulated and can be adjusted to meet a wide range of design and application formats. Here, the purity of color is affected mainly by fuel(s) type and percentage to that of smoke agent(s) employed. The higher the fuels percentage, the "dirtier" will be the smoke purity. However, fuels are necessary for ease of ignition, smoke density and gas production and many are available that meet the requirements placed on them for smoke production to perk a sluggish mixture, suppress heat or flame or increase non-combustible inert gas production to aid the development of evacuating smoke particles. Additional oxidizer with a whitener is often added to help purify the color (by consuming and/or bleaching soot) and lower the ignition point of an otherwise difficult to ignite mixture. Candidate examples are $KClO_3$ or NH_4ClO_4 / ZnO.

EXAMPLE FORMULATIONS & TEST RESULTS

WHITE SMOKE

Ingredient	% by weight	Purpose
Hexachloroethane (HCE)	40-45	gas, smoke (also acts as oxidizer)
Zinc oxide	40-45	gas, smoke whitener, heat suppressor
Aluminum	4-7	ignition, smoke
Sucrose or Dextrose	5-10	ignition, gas, smoke
Potassium chlorate	5-10	ignition, thorough combustion (less ash)

The formulation employs sugar(s) for ease of ignition and smooth burn but they also lend an off-white color to the smoke in the form of soot. Additional ZnO will help purify the color. Here, we add a small percentage of oxidizer to increase combustion of the organic ingredients to help reduce soot and subsequent ash for a cleaner smoke color while reducing the ignition point for simple reliable ignition. Generally, this type of composition contains no additional (conventional) oxidizer (the HCE acts as the oxidizer) but these are notorious for being very difficult to ignite requiring a thermite type ignition prime. Adding a small percentage of potassium chlorate will help eliminate the ignition problems.

COLOR SMOKE

In many color smoke compositions, soot producing agents can be added not to dilute or dirty the color but to enhance it. We will show that hydrocarbons can be added to increase smoke density and volume as well as enrich the color. This is accomplished by supplying a thick cloud of soot upon combustion that is easily colored by the subliming dye thus making the smoke cloud higher density of perceivably deeper hues.

Example formulations

The following formulations for preliminary testing are listed with a constant minimum oxidizer percentage to show the effects of varying ingredients and their percentages.

Test A

Ingredient	% by weight	Purpose
Dye	55.0	Coloration
Potassium chlorate	25.0	Oxidizer
Flour, wheat	5.0	Fuel
Sodium bicarbonate	10.0	Stabilizer, gas, heat suppressor
Sucrose	5.0	Fuel, gas, smoke, ignition

Test evaluation uses a scale of 0-10 (10 being best, larger or faster)

Smoke volume	**8**	**Coloration**	**8-9**	**Flaming**	**0**
Ignition	**10**	**Burn duration**	**7**	**Ash qty**	**8**

The higher quantity of $NaHCO_3$ in the formulation lengthens burn duration while supplying vital unreactive CO_2 which replaces atmospheric oxygen at the reaction surface for better dye vapor release without flaming. An excess of atmospheric oxygen at reaction zone would increase combustion heat to destroy much of the vaporized dye thus diluting or destroying color. Here, a slight increase in oxidizer content to increase combustion volume and likewise smoke volume is possible without destroying the color quality. Increasing surface area of burn will also accomplish this without increasing the oxidizer percentage. Note; Many military formulations contain up to 30% $NaHCO_3$ or other similar heat suppressor.

Test B

Dye	50.0	Coloration
Potassium chlorate	25.0	Oxidizer
Sodium bicarbonate	5.0	Stabilizer, gas, heat suppressor
Sucrose	10.0	Fuel, gas, smoke, ignition
Asphaltum	10.0	Fuel, smoke

Smoke volume	**9**	**Coloration**	**10**	**Flaming**	**0**
Ignition	**10**	**Burn duration**	**8**	**Ash qty**	**6-7**

The presence of a solid hydrocarbon markedly increases both smoke volume and color quality by subliming out of the reaction zone which provides less ash that would otherwise block proper dye vapor release and provides greater smoke production in the form of soot that is easily colored by the concentration of dye particles thus producing the color cloud.

Test C

Dye	50.0	Coloration
Potassium chlorate	25.0	Oxidizer
Sodium bicarbonate	5.0	Stabilizer, gas, heat suppressor
Asphaltum	20.0	Fuel, smoke

Smoke volume	**10**	**Coloration**	**10**	**Flaming**	**1**
Ignition	**10**	**Burn duration**	**5**	**Ash qty**	**6**

The greater percentage of asphaltum lengthened burn duration considerably yet supplied excellent smoke volume and rich color. A slight increase of oxidizer and bicarbonate (ox being the greater) would appreciably enhance operation in a completed device where atmospheric oxygen cannot lend to flaming due to an enclosed reaction and ensuing CO_2 and other byproduct gasses.

Test D

Dye	55.0	Coloration
Potassium chlorate	25.0	Oxidizer
Sodium bicarbonate	2.0	Stabilizer, gas, heat suppressor
Sucrose	8.0	Fuel, gas, smoke
Zinc oxide	10.0	Smoke, gas, heat suppressor

Smoke volume	**9**	**Coloration**	**7-8**	**Flaming**	**0**
Ignition	**10**	**Burn duration**	**8-9**	**Ash qty**	**10**

Zinc oxide provides good smoke volume but as a whitening agent, it diluted the color somewhat (the higher its percentage, the higher the dilution factor). Oxidizer content here could be increased slightly and composition granulated to provide porous ash development, faster combustion and improved smoke color overall.

Test E

Dye	55.0	Coloration
Potassium chlorate	25.0	Oxidizer
Sodium bicarbonate	5.0	Stabilizer, gas, heat suppressor
Sucrose	10.0	Fuel, gas, smoke
Magnesium carbonate	5.0	smoke, gas, stabilizer, heat supp.

Smoke volume	**8**	**Coloration**	**8**	**Flaming**	**5***
Ignition	**10**	**Burn duration**	**8**	**Ash qty**	**8**

Here, the $MgCO_3$ acts to accelerate the combustion rate of a loosely placed powdered composition by acting as an anti-cake agent preventing agglomeration and supplying a higher quantity of atmospheric oxygen within the composition. In open air, the composition will most likely flame and must be placed within a properly constructed case for use. A percentage of solid hydrocarbon such as asphaltum would enhance overall performance. Granulating the composition would also control flaming and supply porous ash development for best results.

Test F

Dye	50.0	Coloration
Potassium chlorate	25.0	Oxidizer
Sodium bicarbonate	15.0	Stabilizer, gas, heat suppressor
Sulfur, flour	10.0	Fuel, gas, smoke, ignition

Smoke volume	**8-9**	**Coloration**	**8-9**	**Flaming**	**0**
Ignition	**10**	**Burn duration**	**8**	**Ash qty**	**8**

Sulfur produces volumes of smoke and gas while supplying a rich slightly deeper color hue. The greater percentage of $NaHCO_3$ is necessary to stabilize and reduce the dangers associated with sulfur / chlorate combinations. In smoke devices, this combination is generally not considered a high risk because of the low chlorate, high neutralizer percentages. The stabilizer content can be equal to that of the chlorate for long term storage. Sulfur / chlorate combinations must be adequately protected from moisture in storage.

D) **Duration of burn;** As the length of burn is controlled by many factors previously discussed, we will spend a bit more time studying perhaps the two most influential of these factors by example as follows;

COLOR SMOKE PRODUCTION

As controlled through
A) oxidizer content
B) composition granulation

On pages 21-23, we express the effects of composition granulation at a constant oxidizer percentage in a particular formulation. Tests A through F (above) show the effects that varying components and ratios of dye to fuel(s) have on the formulation using a constant oxidizer percentage. Here, we will show how to increase smoke production through an increased oxidizer percentage (which also decreases the duration of burn) using a constant percentage of dye. Dye is a diluent in these mixtures - the higher its percentage, the slower the burn rate.

Test 1

Dye	50.0
Potassium chlorate	20.0
Asphaltum	20.0
Sucrose	7.5
Sodium bicarbonate	2.5

Core molded, **light** pressure
Composition; powder
Composition qty; 3 oz
Burn duration; 342 seconds

Lengthy burn duration and low smoke volume (oxidizer percentage is too low). Good color for approximately 170 seconds fading to grey. Percentage of oxidizer is much too low for proper combustion heat to control ash buildup which blocked the escape of vaporized dye. A smaller and more porous ash column would have produced better results. This particular formulation is of no good use.

Test 2

Dye	50.0
Potassium chlorate	22.5
Asphaltum	15.0
Sucrose	10.0
Sodium bicarbonate	2.5

Core molded, light pressure
Composition; powder
Composition qty; 3 oz
Burn duration; 269 seconds

Low smoke volume but an increase over test 1. Good color for approximately 200 seconds fading to end of burn. Very low heat yield and semi-porous ash development (hence, the longer color duration).

Test 3

Dye	50.0
Potassium chlorate	23.0
Asphaltum	15.0
Sucrose	9.0
Sodium bicarbonate	3.0

Core molded, light pressure
Composition; powder
Composition qty; 3 oz
Burn duration; 198 seconds

Low heat and smoke production but increasingly better than previous tests. Steady burn rate and good color throughout burn. This formulation is good for long burn novelty or for use in wind tunnel or smoke markers.

Test 4

Dye	50.0
Potassium chlorate	24.0
Asphaltum	15.0
Sucrose	8.0
Sodium bicarbonate	3.0

Core molded, **medium** pressure
Composition; powder
Composition qty; 3 oz
Burn duration; 241 seconds

Low heat and better smoke production with good color throughout burn. Semi-porous ash development. The increased burn duration over test 3 is a result of increased pressure in molding the grain. The ash column was slightly less porous than test 3 due to increased composition density using powdered composition, again, due to pressure in forming the grain.

Test 5

Dye	50.0
Potassium chlorate	25.0
Asphaltum	14.0
Sucrose	8.0
Sodium bicarbonate	3.0

Core molded, light pressure
Composition; powder
Composition qty; 3 oz
Burn duration; 140 seconds

Excellent smoke volume and color throughout burn. Slightly higher heat yield yet did not burn into treated casing (slight charring only). Ash column was smaller and more porous than that of previous tests.

Test 6

Dye	50.0
Potassium chlorate	25.0
Asphaltum	14.0
Sucrose	8.0
Sodium bicarbonate	3.0

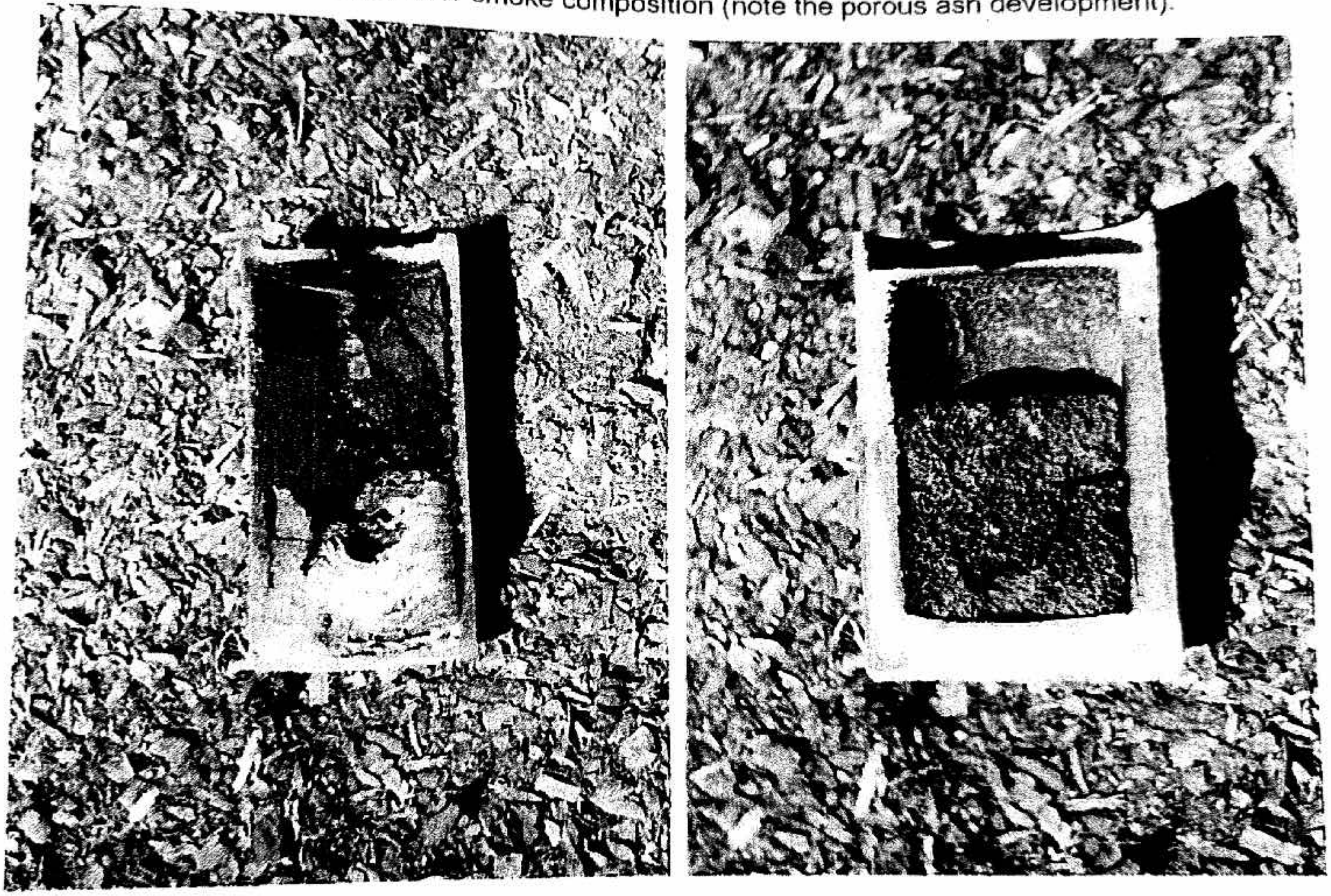
Core molded, light pressure
Composition; **granulated**
Composition qty; 3 oz
Burn duration; 85 seconds

The same composition as test 5 is granulated and loaded using the same procedure and pressure. The result is a large increase in smoke volume and density with a decrease in overall burn duration. Excellent smoke density and color (best of all tests). Ash column was approximately the same size as test 5 but much more porous which provided best vaporized dye particle release during combustion which resulted in improved smoke quality.

Our tests were continued with oxidizer percentages being increased to 30% with the same constant dye quantity. Test 5 proved to be the best color using powdered compositions. When the oxidizer content was increased over 25% (powdered composition) the color started to fade increasingly earlier in the burn as the oxidizer percentage increased. By granulating the composition, good color was achieved through 29% oxidizer levels with burn duration decreasing accordingly. Best smoke color and volume was achieved with oxidizer levels between 25 and 27 percent. We observed no advantage to increasing the percentage over 27% as little change other than higher heat with increased case erosion, short burn durations and diluted color being the results.

E) **Ash quantity and density;** When pre-testing possible compositions for use, the size and density of the developing ash is of particular importance in obtaining optimum smoke production. Compositions that are affected by excessive ash development (most notably color smoke compositions) must be formulated and designed to allow the vaporized material(s) to freely escape through the developing ash to condense with moisture in the air forming the solid particle cloud. Excessive high heat reactions or those producing dense ash columns will detain and destroy much of the vaporizing particles resulting in weak diluted color.

The following photos are examples of properly formed ash columns. On the left is ash from an improved HC smoke composition (note the layer to layer burn configuration) and on the right is ash from a color smoke composition (note the porous ash development).



Good color smoke devices are difficult to design and formulate without understanding how they function. Unlike higher heat reactions such as those produced by hexachloroethane or modified HC which reduce ash through higher combustion temperatures, the mandatory low heat reaction of a color smoke composition is necessary but not adequate enough to reduce ash buildup during combustion which can block up to 70% of the vaporized dye if steps are not taken to provide a loose, porous ash that allows the free escape of the vaporized material(s) with the combustion gasses. Among these steps would be choosing candidate materials that will cool, stabilize and produce a low density, porous ash column.

The following materials are commonly used to formulate both white and color smoke compositions;

- Ammonium chloride
- Anthracene
- Asphaltum
- Cellulose acetate
- Charcoal
- Color dyes
- Corn meal
- Dextrine
- Dextrose
- Hexachloroethane
- Naphthalene
- Nitrocellulose lacquer
- Paraffin
- Phosphorous, red
- Polymers / curatives
- Polyvinylchloride
- Starch
- Stearic acid
- Sulfur, flour
- Wheat flour
- Wood cellulose
- Zinc, dust
- Zinc oxide

White smoke compositions yielding higher combustion temperatures usually evolve less ash than low heat reactions where the higher combustion heat decomposes more of the ash as it forms. These higher heat reactions usually produce smoke through the production of chlorides with byproduct gasses that condense with the moisture in the air forming the white cloud. As with color smoke, the higher the humidity where used, the more dense will be the smoke cloud.

High heat reactions in many smoke compositions may often be reduced by the addition of a cooling agent / stabilizer material such as sodium bicarbonate, zinc oxide, calcium carbonate or magnesium carbonate. The example formulation listed below was composed for the following characteristics;

A) Lower ignition temperature (easier to ignite) and smooth burn
B) Lower combustion heat
C) Increased smoke and gas production
D) Longer storage life

Publicized HC Formulation	% by weight
Hexachloroethane	45.0
Zinc oxide	47.5
Aluminum, powder	7.0

	Improved HC Formulation	
	Publicized HC	70.0
	Potassium chlorate	10.0
	Sucrose	10.0
	Zinc oxide	5.0
	Magnesium carbonate	5.0
(additional %)	Stearic acid	1.5

The addition of sucrose and potassium chlorate provide lower ignition temperatures and smooth burn with an increase of gaseous product and smoke while stearic acid reduces the sensitive frictional nature $KClO_3$ may impose on the formulation. Increasing the oxidizer percentage slightly (1-4%) further reduces the ignition point, reduces ash slightly and supplies smooth smoke generation throughout burn. Additionally, the magnesium carbonate and zinc oxide provide unreactive gas to quench possible flaming and provide white smoke through a "bleaching" effect. Acting as a coolant, they reduce combustion temperature and help stabilize the composition by neutralizing acids formation that may occur with moisture during storage.

Because of the high vapor pressure of C_2Cl_6, and the hygroscopicity of the mixture itself, steps must be taken to minimize the effects that moisture and humidity would otherwise have on the composition during storage. Without these steps, the compositions would have rather short shelf life. These steps would include sealing the exposed surface of the composition within the tube with a solution of NC lacquer/acetone (40/60) or cellulose acetate solution (one ounce CA dissolved in one quart acetone). Once completed with end caps in place, the device is sealed in wax or similar moisture retardant. The better they are sealed, the longer their shelf life will be.

BINDERS & SEALANTS

Pyrotechnic compositions often require an additional agent (binder) to hold the components together in the homogenous blend necessary to support proper combustion and must remain in this state throughout construction, storage and use. Often times, loose compositions employing no binder will separate (one or more components migrating from the mix to the bottom or top of the other components) which will have an effect on the performance of the device in use. A binder simply holds the ingredients together thus preventing this. However, adding a binder usually holds the entire mass together as one which decreases the surface area exposed to burn which would *lower* the combustion rate. To fix this problem the composition containing the binder is moistened with the proper solvent and the "dough" is scraped across a screen to granulate the composition for use (see page 22 for more information).

Binders also act as a form of fuel and as such may tend to decrease the burn rate if added after the fact. If not originally figured in the percentages and tested, adding additional fuel(s) of any kind would reduce the oxidizer percentage in the formulation and thus reduce the burn rate according to the percentage added. Keeping the percentage as low as possible (5% or less) is best. Added as an additional agent, it may be necessary to increase the oxidizer percentage slightly to keep the combustion rate consistent with original test results.

When selecting a binder, solubility is an important factor and must be considered according to the components used. Mixtures employing ingredients that are reactive with water or moisture (such as C_2Cl_6/Zn) should **not** employ binders that are water activated such as dextrine or gum arabic. Here, cellulose acetate or NC lacquer solution is advised (for superrior moisture resistance) or a binder that is alcohol soluble such as red gum or shellac. The binder and its solvent must have a neutral (non reactive) effect in combination with the other components. Note; acetone (and other solvents) are hygroscopic and will absorb moisture in storage if not purged with nitrogen. Before using with reactive ingredients, the moisture should be extracted by adding a tablespoon of granular desiccant per quart of solvent and shake. This will absorb any moisture that may be present before use.

Binders can act as sealants as well to "seal" the exposed composition to the container to protect it from moisture and abrasion. Used as a sealant, they must be resistant to moisture and the effects of humidity in storage. Good candidates for sealants include cellulose acetate solution, NC lacquer solution and vinyl resin solution. The first two are also the better choices for the binder in prime slurries because (used in moderation) they will not affect the ignition point or burn rate of the ignition prime. Desirable properties of a good pyrotechnic *sealant* are as follows;

1) Moisture-proof and non-hygroscopic (water insolubility)
2) Good adhesive properties with a variety of substrates
3) Compatibility to pyrotechnic chemicals in combination
4) Good solubility in fast drying solvents
5) Compatibility with plasticizers to form elastomeric sealants if necessary

BASIC PYROTECHNIC BINDERS/SEALANTS AND THEIR PROPERTIES

Candidate	**Solubility**	**Comments**
Asphaltum	Mineral spirits Toluene Turpentine other solvents	Excellent low cost moisture-proof sealant/binder. Flexible but burns with increased smoke. Softens @ 149 C
**Cellulose acetate (CA)	Acetone For general purpose use, dissolve 1.0-1.125 oz CA in one quart acetone. Thick, heavy concentrated solution is 3 oz CA/qt acetone	Moisture-proof sealant/binder. Solution may be thinned with toluene to slow evaporation rate if needed. **Excellent for use in prime slurries or as sole binder in moisture sensitive compositions. Will not increase ignition points. Can be used to coat metals for protection. Burns easily with no smoke of its own to block visual effects. Add a small % of plasticizer for elastomeric sets. Good sealant
Dextrine	Water	Low cost, slightly hygroscopic, does not moisture-proof. Insoluble in alcohol or solvents. Rigid set
Gum arabic (Acacia gum)	Water	No moisture-proofing properties, insoluble in alcohol, slightly acidic. Not recommended for use with chlorates. Rigid set
Linseed oil	Hydrocarbon solvents	Excellent moisture-proofing properties but slow drying and reduces combustion rate according to qty used. Used extensively as binder for road flares and similar slow burning pyrotechnics. Usually increases ignition points and burns with smoke. Can be used to coat metals.

Candidate	Solubility	Comments
**Nitrocellulose (solid) to make lacquer solutions or Nitrocellulose lacquer (NC)	Acetone	Moisture-proof sealant/binder. Solution may be thinned with toluene to slow evaporation rate if needed. **Excellent for use in prime slurries or as sole binder in moisture sensitive compositions. Can be used to coat metals for protection. Burns easily with no smoke of its own to block visual effects. Will not increase ignition points. Add a small % of plasticizer for elastomeric sets. Commercial lacquer is more expensive than cellulose acetate
Parlon (chlorinated rubber)	Acetone Heptane Xylene	Easier to use in solution form (better solubility), moisture resistant. Good chlorine donor for color flames. Rigid set. More expensive than other binders
Polybutadiene resins (R-45 or Pban)	Un-catalyzed resin thinned with plasticizers, hydrocarbon oils and solvents (where needed)	These require no volatile solvent to evaporate from the mixture which causes shrinkage. Instead, they are *cross linked* using curatives (isocyanates for R-45 and epoxy for Pban). Low smoke production with 65+% oxidizer loadings and moisture-proof qualities. Very versatile. Can be used for most any pyrotechnic application. Compositions can be molded in most any shape or granulated for use and have excellent elastomeric (abrasion resistant) qualities and long shelf life.
Polypropylene resin	Toluene	Use in solution form for moisture-proof, elastomeric sets. Good binder & sealant
Polystyrene resin	Methylene chloride Toluene	Use in solution form for moisture-proof, rigid sets. Good binder & sealant
Polyvinylchloride (PVC)	Methylene chloride Methyl ethyl ketone (MEK) Cyclohexanone	Easier to use in solution form (better solubility), moisture resistant. Good chlorine donor for color flames. Rigid set

Candidate	Solubility	Comments
Red gum (accaroides resin)	Denatured alcohol	Non-hygroscopic, good hot fuel and binder. Rigid set
Rosin	Alcohol Benzene Ether	Good fuel & moisture-proofing binder. Tacky - easier to use in solution form. Burns with smoke. Softens @ 110 C
Saran resin	Cyclohexanone MEK	Best used in solution form. Good chlorine donor for color flames. Non hygroscopic, moisture resistant rigid sets
Shellac (lac resin)	Denatured alcohol	Good fuel, non-hygroscopic. Rigid set. More expensive than other binders yet some formulations require it (no substitutions) to get good results
Sodium carboxymethylcellulose (CMC)	Water	Good binder with as little as 1%. Used as a thickening agent (gelling agent) for match slurries, etc. Rigid set
Starch	Hot water	Low cost. Purported to help minimize the effects of moisture
Vinyl resin (40% solids solution)	Toluene MEK acetone	Good binder with "tacky" adhesion while wet for specialty applications. Also used as the final coat over electric match heads. Crystal clear elastomeric sealant

Compositions that require casting into particular shape(s) or "grains" should employ a binder which has been figured in the formulation percentage - not an addition to a working formulation. Such an addition may have an effect on the ignition point and burn rate of the original mixture. However, weak binder solutions may be employed to moisten a powder composition for casting or the solution "spritzed" onto a formed grain to keep it in tact. Providing the solids loadings of the solution are low enough, the addition will have little or no effect on the physical properties of the mix. One of the best adhesives I have found for this is **cellulose acetate**. For general pyrotechnic use, 1.0-1.125 oz CA is dissolved in one quart of acetone for use. Cellulose acetate will not affect the ignition point or combustion rate of the original mixture when used in moderation.

IGNITION & DELAY

IGNITION

Simple, thorough ignition is a must for reliable smoke generating devices where many compositions have high ignition points requiring hot, thermic igniters as a first fire prime.

Compositions designed to produce smoke are also designed with lower than normal oxidizer contents to control burn rate and subsequent combustion heat that contributes to flaming. If flaming occurs, both volume, density and color of the smoke is destroyed. Although there are a number of ways to control this, the most logical is that of low oxidizer contents and coolants to absorb excess heat. However, there is a down side to low oxidizer contents in pyrotechnic compositions. The first and foremost is high ignition points. Unfortunately, by increasing the oxidizer content in an effort to reduce ignition points, will decompose more of the vaporized smoke producing agent(s) lowering smoke density and increase combustion heat and case erosion. Here, the use of a low melting point oxidizer is the best choice.

One of the most commonly used oxidizers in smoke compositions (mainly color smoke) is potassium chlorate. It has a low melting point (356°C) supplying a lower ignition point and lower combustion heat than other conventional oxidizers and the low percentage (usually below 30%in smoke compositions) does not increase the sensitive natures to unacceptable levels that come hand in hand with higher percentages of chlorate.

Whenever high ignition points are involved, the use of a hot thermic prime is used to ignite the composition reliably. Such a prime contains agents, a combination of which, is easily ignited by normal means and combust to form high energy (heat) and solid molten particles (slags) that "melt" into the main composition to effectively initiate the ignition process. Once combustion is started, the reaction (adequately supplied with combustible fuel(s) and oxygen) is sustained by an atmosphere of increasing pressure and heated ash.

Requirements placed on prime mixtures include properties to;

A) Ignite easily by normal conventional means and supply exothermic values high enough to quickly initiate heat transfer and sustained combustion.

B) Be compatible with other components and stable during manufacture and prolonged periods of storage at various temperature and atmospheric ranges.

C) Propagate slowly to supply necessary thermic values with a minimum energy release of combustion spatter, gas and light (to minimize possibilities of spot fires in use).

D) Sustain combustion throughout main reaction by supplying adequate molten "slags" to transfer heat to unburned composition beneath the initial reaction surface.

E) Be non-hygroscopic, indeed, supply protective moisture-proof barrier for sure fire ignition in foul weather and adverse storage conditions (through the use of a moisture resistant resin such as cellulose acetate).

Unlike most other pyrotechnic compositions which contain oxidizer percentages in excess of 55-60% which allow for low ignition points for easy ignition and rapid combustion rates, as stated, smoke compositions must generate low combustion temperatures made possible by oxidizer percentages at levels barely adequate to initiate combustion and enough gaseous products to carry vaporized combustibles freely from the reaction and further decomposition by excessive heat or open flame.

Compositions of low oxidizer and high diluent contents such as smoke compositions can be inherently difficult to ignite and must therefore be supplied with stimulus such as a thermic prime to transfer heat well into the surface of the composition and maintain this heat (from molten solid "slags") until sustained combustion develops. An example of such high ignition points (well over 800° C) is hexachloroethane/zinc or zinc oxide/aluminum. These cannot be ignited without the use of a thermic prime of high molten solids under combustion.

A list of candidate materials for smoke and priming compositions include the following;

Oxidizers

- Barium nitrate
- Barium peroxide
- Potassium chlorate
- Potassium nitrate
- Potassium perchlorate
- Sodium nitrate

Also included, acting as high temperature oxidizers are;

- Hexachloroethane
- Iron oxide
- Lead dioxide
- Red lead tetraoxide

Fuels

- Antimony sulfide
- Carbon (charcoal)
- Dextrose
- Lactose
- Sucrose
- Sulfur

Thermic agents

- Aluminum
- Antimony sulfide
- Iron oxide
- Magnesium or magnallium
- Manganese dioxide
- Silicon

Binders (also act as fuels)

- Asphaltum
- Cellulose acetate (solution)
- Dextrine
- Nitrocellulose lacquer (solution)
- Red gum

Cooling agents/stabilizers (Diluents)

- Calcium carbonate
- Magnesium carbonate
- Sodium bicarbonate
- Zinc oxide

Color agents

Ammonium chloride
Color dyes & pigments
Zinc oxide
Chlorides (combustion by-products)

Prime compositions

By carefully selecting candidate materials, a variety of prime mixtures with varying thermic values and combustion rates as required by the particular composition can be produced. Below are example compositions which are listed in order of their thermic value (heat and slag generation). The latter compositions are best used for high ignition point compositions.

A)	*Sodium nitrate	51.0 % by weight
	Sucrose	41.0
	Charcoal	8.0
	Cellulose acetate, solution	to make a slurry

* Sodium nitrate is hygroscopic. Do not use a water soluble binder to make the prime slurry for use.

B)	Potassium nitrate	70.0 % by weight
	Charcoal	20.0
	Red iron oxide	6.0
	Dextrine	4.0 (water)
C)	Potassium perchlorate	60.0
	Silicon	15.0
	Aluminum, 40-270 mesh	8.0
	Charcoal	4.0
	Red iron oxide	3.0
	Red gum	10.0 (denatured alcohol)
D)	Barium peroxide	50.0
	Potassium perchlorate	20.0
	Aluminum, 40-270 mesh	5.0
	Magnesium or magnallium (approx 100 to 200 mesh)	15.0
	Red iron oxide	5.0
	Black iron oxide, medium fine	5.0
	Cellulose acetate solution	to slurry

The combustion rates of these mixtures may be adjusted by adding or subtracting the oxidizer percentages (subtracting or adding the same amount of fuels). The higher the oxidizer percentage, the faster the combustion rate.

Time delays

Although priming doubles as a slight delay before ignition of the main composition, there are other ways to produce longer, controlled time delays when needed.

The use of a friction igniter or "pull string igniter" allows a variety of delay possibilities including direct, instantaneous ignition of the main composition using a length of quick-match or black-match (braided cotton yarn impregnated with black powder) which burns very rapidly, almost instantaneous. For longer delays, a length of safety fuse is used. This type of fuse is braided and coated to supply a slower combustion rate which is quite reliable. The longer the fuse, the longer the delay.

The friction igniter contains a short tube or "barrel" to which the fuse or match is inserted. This tube is then epoxied to the sidewall of the smoke container, usually on the inside just above the composition grain. The other end of the fuse or match is "cemented" into the main composition with prime slurry. Again, the length of fuse determines the delay time.

The igniter may also be mounted on the outside of the container as well to suit the particular design and type of device but this design has its drawbacks. The safety fuse is not protected and can ignite spot fires if used in dry grasses or other combustibles.

The use of pull string ignition is most common and highly desirable in survival and other applications where matches may be in short supply and reliable, wind-proof ignition is a must. On the other hand, just a length of safety fuse and a cigarette lighter can be used as well but as explained, this type has its limits and finds its use more in firework applications than signaling or survival use.

SMOKE CANDLES & SMOKE STARS

Many compositions designed for use in pellet form (classification 1 & 4/A page 7) usually contain slightly higher percentages of an oxidizer with fuel(s) that produce smoke from their rapid combustion. The smoke, largely a solid byproduct from the pyrotechnic reaction can produce rather poor results as compared to the formation of metal chlorides and moisture. However, the light weight smoke of lower density has its applications as well. An example of a smoke candle that may be used for both wind tunnel use, fungicide for nurseries and rodent control (from the high concentration of sulfur dioxide produced) is as follows;

A)	White	Potassium nitrate	48.0 % by weight	oxidizer
		Sulfur, flour	44.0	fuel, smoke
		Charcoal, air float	5.0	fuel, combustion
		Dextrine (water)	3.0	fuel, binder

Here, the sulfur sublimes to form solid particles with strong sulfur dioxide gas (SO_2) aided by charcoal for a smooth combustion. The high oxidizer content is required for sustained combustion of the sulfur as well as ease the ignition. Unlike color smoke, the high heat produced does not destroy the quality of smoke produced from this type of reaction and no special container is necessary, indeed, the formation of pellets with no outer wrap is common practice. Rather difficult to ignite, they require a hot pyrotechnic prime for proper ignition.

Another form of smoke can be produced from the incomplete combustion of organic fuel(s) such as the production of soot. Volatile solids of high carbon content are good candidates for soot production. The following formulation is an example of such a reaction;

B) Black	Potassium perchlorate	55.0 % by weight	oxidizer
	Sulfur	11.0	fuel, smoke
	Naphthalene (or anthracene)	30.0	fuel, soot
	Asphaltum (mineral spirits)	4.0	fuel, binder, soot

An example of a different type of composition that contains no conventional oxidizer is that containing red phosphorous. The combustion of phosphorous and metallic fuels produce oxides that strongly attract moisture in the air forming a dense white smoke cloud. Phosphorous ignites very easily without a conventional oxidizer and there are many formulations currently being explored. The combination of phosphorous and *any* conventional oxidizer would render the mixture highly sensitive to friction, shock or heat and will become unstably explosive! Note; The combustion of phosphorous produces acidic/toxic phosphoric acid and is not recommended for use where direct contact will be made.

C) White	Red phosphorous, amorphous	55.0 % by weight	fuel, smoke
	Manganese dioxide	30.0	fuel, combustion
	Magnesium (coated)	7.0	fuel, smoke
	Magnesium carbonate	1.0	stabilizer
	Cellulose acetate (solution)	to slurry	binder

The magnesium is coated prior to adding to the mixture for protection in storage. Devices made from this composition must be sealed from moisture.

Fumes from burning phosphorous are toxic and compounds containing it are extremely sensitive to heat, friction or spark and highly reactive when in contact with oxidizers or sources of oxidizers such as prime compositions. Phosphorous is ***too reactive*** to be used safely and it is therefore the opinion of this author that it should be avoided. We offer this formulation for information purposes only.

Color smoke compositions can also be used in compressed pellet form but it is best to press the composition into a thin wall paper tube open at both ends. A hole is formed through the grain end to end and fused with a length of match and the ends are sealed with a moistureproof prime composition. This will supply enough surface area to produce good color, otherwise, burning from one end produces a much smaller column of smoke. It is sometimes necessary to increase the oxidizer content for pressed pellets in order to overcome the lack of burn surface created by compression yet not high enough to cause flaming which will destroy color. An example formulation follows;

D) Violet	Rhodamine B	47.0	color dye
	Potassium chlorate	27.0	oxidizer
	Sucrose or dextrose	13.0	fuel
	Sodium bicarbonate	13.0	stabilizer, coolant
	Cellulose acetate solution	moisten mix to press	binder

Smoke pellets are also used to create daylight aerial shells. The smoke is pressed into pellets with no wrap and coated with priming. They are loaded into shells in the same manner as stars. Upon ignition, the burst charge ignites the stars and splits the shell throwing a colorful display of smoke trails as they descend. The following are examples of smoke stars taken from Shimizu. They may have slight changes to suit product availability;

E) White chrysanthemum (non-dye)

Potassium nitrate	53.0	oxidizer
Sulfur, flour	7.0	fuel
Charcoal, air float	32.0	fuel
Lampblack	8.0	fuel
Dextrine solution (water)	to moisten	binder

F) Black (non-dye)

Potassium perchlorate	56.0	oxidizer
Naphthalene (moth balls)	33.0	fuel, smoke color
Sulfur, flour	11.0	fuel
Dextrine solution (water)	to moisten	binder

G) Green (dye)

Potassium chlorate	33.0	oxidizer
Sucrose (milk sugar)	27.0	fuel
Oil yellow	20.0	fuel, smoke color
Phthalocyanine blue	20.0	fuel, smoke color
Cellulose acetate solution	to moisten	binder

H) Yellow (dye)

Potassium chlorate	32.0	oxidizer
Sucrose (milk sugar)	28.0	fuel
Oil yellow	40.0	fuel, smoke color
Cellulose acetate solution	to moisten	binder

I) Blue (dye)

Potassium chlorate	33.0	oxidizer
Sucrose (milk sugar)	27.0	fuel
Phthalocyanine blue	40.0	fuel, smoke color
Cellulose acetate solution	to moisten	binder

Once pressed and dried thoroughly, the stars are coated with a prime slurry and dried. When working with dyes, wear rubber or latex gloves and cover the table with newspapers. Dyes are messy to work with and will stain hands and equipment.

Test the stars by firing from a star gun. If the stars flame (except formulations E & F) reduce the oxidizer 1-2%.

"EXPLOSION OF SMOKE" & TRAILING COMPOSITIONS

The term "explosion of smoke" has been used to explain the abrupt production of smoke from a high energy composition. Certainly the most widely known of these high energy mixtures is *flash mix*. Usually a mixture of strong oxidizer (potassium perchlorate) and aluminum, the smoke produced from the rapid superheated combustion consists mainly of potassium and aluminum oxides dispersed and mixing with moisture in the air forming light gray/white smoke. These formulations for years have been employed in military simulator and white light flash devices called *flash bangs*. These compositions can be altered to enhance various properties for use in theatrical special effects. The addition of easily reduced materials that are vaporized in the heat of combustion will add to the density and color purity of the smoke produced and reduce the combustion rate slightly according to the quantity added to the flash mix.

For white smoke, two agents can be added which will increase the density, volume and whitening of the smoke. These two are ammonium chloride and zinc oxide. An example of this is as follows;

A) White flash & smoke

Potassium perchlorate	63.0	oxidizer
Aluminum, dark flake	23.0	fuel, smoke
Ammonium chloride	7.0	fuel, smoke color
Zinc oxide, powder	7.0	whitening agent

Increasing the ammonium chloride will slow combustion rate and supply more smoke. The zinc oxide cools and whitens the smoke by attracting and consuming the carbon produced during combustion which would otherwise tint the smoke gray.

Black powder modifications

Compositions similar to this and others can be modified to meet the requirements of theatrical and special effects for compositions that "trail", that is to say they burn in the patterns they are placed in as small thin trails. We have all seen black powder used this way but black powder may burn too rapidly for particular applications. Mixtures of black powder and a combustible are used widely in special effects. We have all seen explosions and fireballs of flame and thick black smoke in the movies. This is the result of the combustion of two ingredients - black powder and granulated Anthracene. The black powder is the propellant and the anthracene (solid hydrocarbon) supplies thick rich black smoke. Sometimes a small bladder of gasoline is added to increase the flame front. The resulting "explosion" is directed upward using a heavy steel flash pot or trough and lasts only a moment or two. The resulting smoke cloud looks like an oil refinery fire or burning rubber.

The combustion of black powder gives off large amounts of gaseous product and smoke making it a good propellant choice for special effect applications. Other ingredients may be added to adjust its burn rate, supply color flame or increase smoke. The possibilities are endless.

The following procedures are examples to add color to the combustion flame of black powder. This can be used as a "trailing" composition, a propellant to produce blank ammunition with color flash or to lift anvils off the ground (anvil firing).

B)	Red flame	Black powder, granulated	85.0 % by weight
		Strontium carbonate	15.0
C)	Blue flame	Black powder, granulated	85.0
		Copper oxide, black	15.0
D)	Purple flame	Black powder, granulated	85.0
		Strontium carbonate	9.0
		Copper oxide, black	6.0

The addition of a chlorine rich agent will deepen the color so it does not "wash out". This can be done by adding an additional 8% or so of PVC (polyvinylchloride) to the mixture but at a price. Remember, each item you add to the black powder will slow the combustion rate according to the amount added. Try small test batches to see if it will work for your particular application.

Another method can be used to formulate black powder mixtures to *increase* the combustion rate. However, be cautious when using *any* of these modifications as propellants. They are not a substitute for black powder for any conventional application. Each has properties unique to the particular mixture and adequate/complete testing as per the application is mandatory. The following method may be used;

E)	Red flame	Black powder (commercial)	62.0
		Strontium carbonate	13.0
		Potassium perchlorate	14.0
		Polyvinylchloride (PVC)	8.0
		Dextrine	3.0

With stirring, add enough boiling water to the black powder to make a smooth batter-like slurry. Continue stirring while adding the other ingredients and mix until well homogenized. If too thick to mix, add a few drops of water. Do not add too much water. The mixture should be like putty or play-dough for further processing. If not, wrap the mass in a coffee filter and squeeze out the excess water. Pack the "dough" into a ball and rub it across a 10 mesh screen over newspaper to granulate. Allow the granules to dry thoroughly in the sun before testing. Adding more potassium perchlorate (subtracting same from black powder) will *increase* the combustion rate. The opposite may also be used to decrease the combustion rate.

The mixing and/or modification of high energy mixtures such as these require great care and experience. Disaster awaits the inexperienced or careless! These compositions are extremely reactive and sensitive to a wide variety of stimuli including heat, friction, static spark and other sources of ignition and as such must be treated with respect. Only small test batches (10 grams or less) should be made at a time. Larger quantities must be mixed by remote means. The use of leather gloves, chemical safety glasses/goggles with polarized lenses if possible (face shield preferred) and long sleeve cotton clothing is a must when working with high energy mixtures. You would be surprised at just how damaging ultra violet light radiation from the combustion of metallic high energy mixtures can be to the skin and eyes ***even at a distance!!***

High energy metallic compositions

As previously explained, a familiar example of perhaps the most widely used, oldest known high energy composition is common black gunpowder. Its combustion produces large volumes of gases and smoke which is a byproduct mainly from the burning sulfur and it has hundreds of uses throughout the industry.

Although black powder can be modified in a number of ways to affect the combustion rate or visible/audible traits during production, to suit particular applications the combustion rate is controlled mainly by its granulation size.

Other mixtures may be formulated for different reasons such as combustion rate, combustion heat, smoke and gas volume or sensitivity to various stimuli including ignition points. The following examples are listed according to their (trailing) rate of burn using a consistent granulation size for each test;

Formulation A)	Basic black gunpowder (commercial)	(Gray/white smoke)
Formulation B)	Slight increase in smoke and burn rate	(White smoke)
Formulation C)	Increase in burn rate, gas and heat	(White smoke)
Formulation D)	High chlorate content - extremely sensitive to heat, friction, static spark, etc. Rapid burn rate	(White smoke)

The purity of smoke produced from tests B, C & D was improved by the addition of ammonium chloride and zinc oxide. Both would be considered diluents in most formulations including these tests but as components in high oxidizer, high energy mixtures, they increase smoke volume and whiten the smoke by consuming atomic carbon during the burn.

	Slower	A	B	C	D	Faster
Oxidizers						
Potassium nitrate		75.0	40.0			
Potassium perchlorate			35.0	64.0		
Potassium chlorate					67.0	
Fuel / smoke						
Charcoal		15.0	12.0		10.0	
Sulfur, flour		10.0	6.0			
Lactose				10.0	9.0	
Aluminum				15.0		
Diluent / smoke / color						
Ammonium chloride			5.0	8.0	10.0	
Zinc oxide			2.0	3.0	4.0	
Binders						
Dextrine *(solution)			+			
Cellulose acetate solution				+	+	
Smoke production (scale 1 to 10)		3+	5	7	6	

* Binder solution is a mixture of water with approximately 10 to 15% dextrine dissolved in it. The mix is moistened with enough of the solution to make it a "dough" for granulating. Caution! Chlorate compositions are sensitive to friction and should be "pushed" through a screen instead of rubbed across it for granulating. The dry "worms" are gently crushed into pieces with a wood block then screened for size. In dry climates (usually high static buildup) it may be better to use dextrine solution for test C & D as well.

Designed more to "trail" than smoke, these formulations require high oxidizer contents to propagate smoothly and continually and as such, the resulting higher heat is responsible for the slight differences in smoke volume and density over standard smoke compositions. The burn rate and smoke volume of the above formulations is controlled by adjusting the oxidizer to diluent ratios (granulation size held constant)) or "fine tuning" by granulation sizing thereafter.

Bear in mind that these mixtures (granulated or powder) are **highly flammable** and become **explosive** when confined (rapid gas evolution)! Production and storage must be according to local, state and federal laws!

INSECT & RODENT CONTROL

For many years, smoke producing compounds laced with insecticides or poisons have been used successfully to fumigate and eliminate burrowing animals (mice, rats, squirrels, skunks, chucks, coyotes, etc) by eviction, suffocation or inhalation of poisonous fumes.

Combustion of mixtures designed to produce noxious or toxic gasses and smoke, pressed into pellets or candles, ignited and placed within the confines of the infestation will expertly eliminate the pest(s) in most cases quickly and thoroughly. The active ingredients are vaporized by the combustion heat of the fuels and carried from the reaction zone with other combustion byproduct gasses and dispersed into the air.

Similar compositions laced with volatilizable insecticides can also be used effectively to control insects and bacteria, etc in greenhouses, barns, storage areas, cellars and even between walls. Mists and smoke have the advantage of reaching into non-accessible areas such as cracks, crevices, between walls, in and around foliage, etc. that liquid sprays cannot reach and insects and bacteria grow and breed. This was the thinking behind the development of household and agricultural foggers and atomizers that release fine mists designed to penetrate hard to reach areas. Although effective, these devices are only capable of treating surface areas that the "mists" fall onto and kill only those that come in direct contact with the liquid agent(s).

Compositions designed to produce toxic gas or insecticidal smoke have the advantage of rich density to penetrate and saturate the infested area(s) leaving a residual coating in places not treatable by other means. Such devices can also be ignited upwind of a potential camping area and allow the smoke to be carried through the site to rid it of flies, biting insects and moths taking refuge in the grasses and foliage. I have used these devices in this manner successfully in my favorite camping area. The device I use contains about 3 ozs of composition with a burn time of approx 60 seconds. A slight breeze carries the smoke across the area.

Compositions employing agents which upon combustion, release toxic gas, insecticides or fungicides with smoke are effectively used to control many types of flying, crawling or burrowing insects and larvae (through fumigation) as well as vertebrate pests or various plant fungus in enclosed areas. These devices are simple and easy to construct and use. The following example formulations are pressed lightly in thick wall tubes previously treated on the inside with lacquer or wax so the liquid insecticides do not absorb into the paper. A slight shallow center core is also formed in the composition and sealed with cellulose acetate solution to retain the shape of the grain. They are ignition primed and fused for use.

PEST CONTROL SMOKE FORMULATIONS

INGREDIENT	A	B	C	D	E
Potassium chlorate			25.0	25.0	
Potassium nitrate					30.0
Sodium nitrate	65.0	43.0			
Asphaltum			5.0		
Cellulose, wood or paper				5.0	5.0
Charcoal, air float	31.0	13.0			2.0
Diatomaceous earth					8.0
Sucrose			5.0	5.0	
Sulfur, flour	4.0	9.0			55.0
Ammonium chloride		5.0			
Hexachloroethane (HCE)			52.0	43.0	
Insecticide (*=additional)		18.0		* 12.0	* 12.0
Magnesium carbonate		7.0	2.0		
Zinc oxide			11.0	22.0	

Note; These formulations may be difficult to ignite depending on the insecticide used. The concentrated varieties used by farmers are best. The higher the concentration, the less you need to use. If too much liquid is added to these formulations, they may not ignite at all.

Check the active ingredients on various household insecticides for type and concentration. You will see a surprisingly low active ingredient percentage. This should give you some ideas. Use full strength for these devices. Do not dilute any of the active ingredients used.

Composition A) Producing mainly carbon monoxide, it is effective for treating burrowing vertebrates ranging in size from mice to coyotes by adjusting the burn duration (subsequent composition weight) as per the size of the nest or den to be treated. The amount of composition will vary from 75 to 300 grams accordingly.

Composition B) Generating more variety of toxins (SO_2, CO, CO_2, etc) including those from a chosen active ingredient (pesticide) to rid an area of both insects and small rodents. Here, the liquid insecticide concentrate is absorbed into the composition. Containers must be treated on the inside to repel the liquid agents thus keeping them in the composition where they can be vaporized by the combustion heat.

Composition C) Employing C_2Cl_6 issuing strong chlorine and other gasses which can be used against a wide variety of crawling insects and burrowing rodents.

Composition D) This employs an additional pesticide for specific or variety control. The pesticide is added to the main composition before pressing into the casing. Again, oxidizer content may need to be increased slightly in order to obtain a smooth burn with a minimum of heat. Good for use on both insects and rodents as per the active ingredient used.

Composition E) This composition employs a specific pesticide with SO_2 for variety control of insects and small rodents with dense coverage. Diatomaceous earth acts as an absorbent and combustion catalyst.

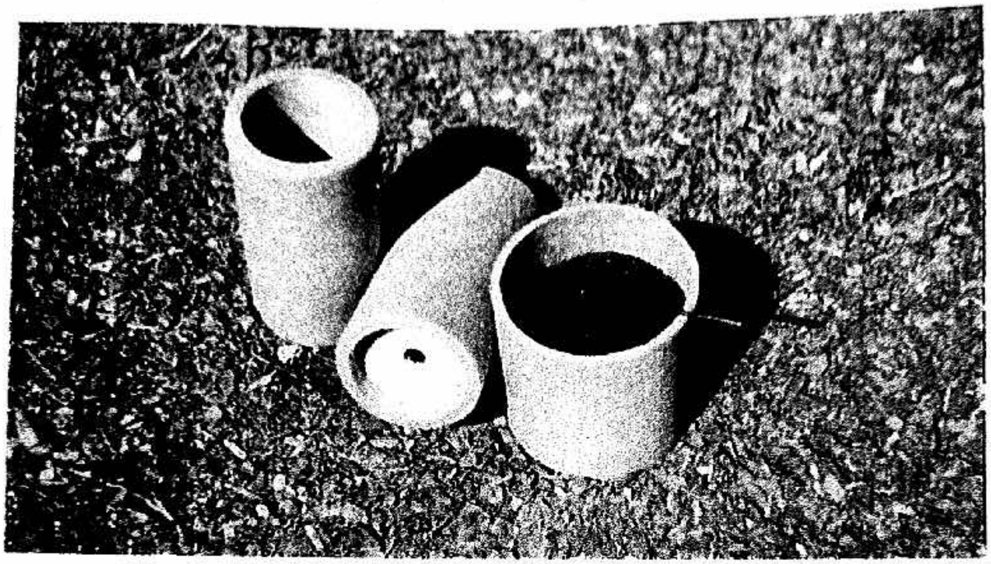
In addition to pesticides and poisons, fungicides may also be employed in the same manner for control of molds and mildew in musty or moist areas where proper ventilation is a problem.

Greenhouses, produce areas and fruit cellars have used sulfur dioxide gas (SO_2) to rid the area of rodents, insects, bacteria and fungus. The SO_2 is generated by combustion of a pyrotechnic composition containing a high percentage of sulfur pressed into pellets or candles of varying burn duration as per the size of the area to be treated. Common size candles consist of 250 to 500 grams of composition and several may be used to treat larger areas.

Although effective, these candles often times merely repel rodents but will kill if they are trapped in areas where they cannot escape the gas. An ongoing program of treatment is most effective for permanent results. The following are example formulations;

	A	B	
Potassium nitrate	25.0	18.0	oxidizer
Potassium perchlorate		7.0	oxidizer
Sulfur, flour	70.0	70.0	active ingredient
Magnesium carbonate	1.0	1.0	stabilizer
Charcoal, air float	2.0	2.0	ignition/smooth burn
Cellulose acetate solution	additional	additional	binder

Both mixtures are rather difficult to ignite (B slightly easier) and require a good prime. After compression and thorough drying, the pellets are dipped into cellulose acetate solution (1 oz CA/quart acetone) and dried before priming. This seals and prevents moisture absorption in storage. The composition is pressed into pellets without a casing (other than outer sealant) because of the negative oxygen balance of the composition which requires free, open access to air in order to burn properly. The addition of $KClO_4$ is minimal and we list it only to show a possible, although slight, increase in combustion rate and ease of ignition. Replacing larger percentages of KNO_3 with $KClO_4$ is possible but comes with an increase in combustion heat that may cause obvious damage. Keeping the percentage as low as possible is best.



SMOKE PRODUCTION & INSECT CONTROL USING VOLATILIZED LIQUIDS

The idea of volatilizing liquids to produce smoke is not a new one. Military units around the world have used this method to produce dense smoke screens to obscure troop movement or buildup or to confuse the enemy forces. Landing craft, armored vehicles and other equipment produce the smoke cloud by pumping diesel fuel or mineral oil directly into the superheated exhaust system where the oil vaporizes into microfine particles which condense with the moisture in the air forming a dense white cloud. Oil based color smoke dyes may also be mixed with the oil to produce color smoke trails. We have all seen the air force and navy flying teams producing color smoke trails at air shows.

This same principle is used to fog large areas to control mosquitos and other flying and crawling insects. The pesticide is mixed with mineral oil and injected into a superheated chamber or small tubing wrapped around the muffler or a propane fired heat source. The ensuing vapor contains billions of microfine "droplets" of active pesticide settling on virtually everything in its path. Here, the pesticide is chosen for quick knock down or a longer term residual effect. As a child I remember the city trucks driving through the neighborhoods fogging for mosquitos and biting flies in the heat of summer evenings. The high volume of smoke produced drifted throughout the neighborhood engulfing everything in its path driven by a slight breeze. It is a very effective way to rid the area of flying pests.

A *pyrotechnic* reaction can also be used to vaporize an oil for smoke production. The oil can either be placed in a cylinder and vaporized by a surrounding thermic reaction or mixed directly into an absorbent mixed with a thermic composition.

The following hydrocarbons may qualify as candidate base materials;

Oil base; Diesel oil, fuel oil, kerosene, mineral oil, mineral spirits, turpentine

Water base; Glycerine

Out of these, there are two that would pose the least health risk when breathed and pumped into a heated system, the least volatility (flammable risk).The first is glycerine followed by mineral oil as the runner up. Both of these can be used to create smoke clouds by themselves that would pose very little health risk when used in an area where it will be breathed in such as military training or special effects stage or theatrical work. The U.S. military now uses "fog oil" which is mineral oil and special effects pyrotechnitions use glycerine mixed with water. Both are superheated to vaporize the oil which condenses in the air forming the cloud. Glycerine water fired with a fogger over ice creates a "smoke" that stays on the floor. Anyone watching "thrillers" on TV has seen this done.

Mixtures containing a solid hydrocarbon and appropriate solvent are also included as candidate materials for similar use. As example, a solution of solid organic dissolved in an aromatic solvent is used as the volatilizing mixture to produce a dense cover cloud. Pesticides and other active ingredients can then be added for a customized effect in addition to smoke cover. Example;

Asphaltum	0 to 20 %
Mineral spirits	20 to 40
Active ingredient	0 to 20
**Mineral oil	10 to 40

** The mineral oil is added to modify the burn rate, the formulation flammability (solvent dilution) or the viscosity of the mixture. The amount of asphaltum is adjusted according to the desired viscosity and volatility required. The higher its percentage, the;

A) Higher the viscosity (reduced fluidity)
B) Slower the combustion rate
C) The higher the density of the smoke
* D) Higher the flashpoint (temp at which auto-ignition occurs)
* E) Higher the ignition temperature
F) Higher the hydrocarbon molecular weight (more smoke)

* Replacing a percentage of toluene with mineral oil will also raise the ignition temp and flashpoint but the solvable mixing time is lengthened. The higher the flashpoint, the less volatile the mixture becomes. To add the mineral oil, it should be dissolved in the solvent <u>after</u> the asphaltum and <u>before</u> additional ingredients are added.

The viscosity of the mixture is important. It must be fluid enough to run (pump) easily through the fogging unit from holding tank to vaporizing chamber, coil or manifold without restriction. Naturally, a mixture designed for a larger system may have to be reduced in viscosity for smaller hand held foggers. If powdered pesticides are added, the mixture may require more solvent or modifying oil to maintain proper viscosity.

In solution, the asphaltum provides smoke by combustion (pure hydrocarbon) dissolved in the solvent which (with or without mineral oil) vaporizes by superheating above the flashpoint in a negative oxygen atmosphere. The addition of mineral oil reduces flammability yet provides good smoke by vaporization and condensing in combination with other combustion gasses. As stated, its percentage is adjusted according to the desired combustion characteristics required by the heating vessel (fogger) and subsequent heat available as generated by its heat source.

Combinations of mineral spirits (lower flammability/higher flash point) with mineral oil or just plain mineral oil is also possible. Mineral oil alone (or mixed with smoke dyes) are commonly used by the military. Used alone, the volatilization of mineral oil is considered the least risk to health out of all smoke generating solutions or solid pyrotechnic compositions.

Similar mixtures can be used with an oxidized material to produce white smoke by condensation. The reaction vaporizes the oil which then condenses with moisture forming the "cloud" of micronized solid particles suspended in the air. Additional ingredients can be added to increase smoke volume and/or purify the color. Example formulation as follows;

Asphaltum	15.0	% by weight
Toluene or mineral spirits	20.0	(additional)
Mineral oil	15.0	
Zinc oxide	24.0	
Cellulose (wood meal or paper pulp)	20.0	
Potassium chlorate	26.0	

This formulation is a basic starting point and may be adjusted in a number of ways to suit a particular requirement. The percentage of oxidizer can be increased if the mixture is difficult to ignite or if the combustion rate is too slow (the opposite also applies). The cellulose is an absorbant and can be adjusted to accommodate fluid volume. Zinc oxide acts as a bleaching agent to purify the (white) smoke color and it too can be reduced slightly to adjust the burn rate or reduce the ignition point. Other materials can be added to customize the formulation such as ammonium chloride which provides good white smoke while reducing the combustion heat if required.

The procedure is basically the same as listed previously. The asphaltum is dissolved in the solvent followed by the mineral oil. The other ingredients are added, mixed homogeneously then pressed into the container. The mixing process should take a bit of time to allow some of the solvent to evaporate from the mix. The mass is then pressed into place while it is still pliable and set aside to allow the rest of the solvent to evaporate before priming, fusing and placing the end caps or plug to finish the device. This composition requires a core through the center of the grain for volumes of smoke.

Although not a true composite (it does not crosslink to form the binder matrix), it can be referred to as a form of composite because the asphaltum, solvent and mineral oil (plasticizer) gel to an elastomeric, moisture resistant resin base as the solvent evaporates. Asphaltum may be increased slightly to form a more rigid set.

COMPOSITE SMOKE FORMULATIONS

In recent years, there has been a lot of effort to develop smoke formulations immune from long term storage effects and unpredictable, adverse atmospheric conditions. Since conventional pyrotechnics are notoriously sensitive to a variety of stimuli during storage, the logical approach to designing pyrotechnic formulations for the future are those that contain some or all of the following properties;

1)	Ease of production	a- low process liability b- inexpensive low tech process equipment
2)	Shrink control	a- true composite "cross-links" using a curative to form the polymer matrix. No solvents or water to evaporate which causes shrinkage
3)	Flexural strength	a- elastomeric binder matrix to absorb minimal shock and expansion/retraction of grain during seasonal changes (heat and cold variables) b- retain grain shape and bond strength with casing c- ability to be cast or molded into shape without the use of a permanent casing (if required)
4)	Moisture resistant	a- non-hygroscopic, indeed, moisture repelling insulating binder matrix (generally rubber base)
5)	Corrosion resistant	a- liquid polymer coats / insulates susceptible materials from conditions of corrosion or decay
6)	Stabilized composite	a- rubber composite "insulates" the ingredients from heat, abrasion, mechanical stress and moisture which increases shelf life and reduces the dangers of heat and cold in storage. Indeed, composite pyrotechnics are generally harder to ignite requiring primes

There are many candidate materials that can be used to form elastomeric, moisture-proof binders that will supply some or all of the above listed properties. The following example candidates were chosen and tested for their ease of use, weatherproofing capabilities and low cost. Properties for each are also listed; Legend: * indicates the properties are possible on a limited scale depending on percentage of resin used and other factors.

Resin	Properties	Extender	Elastomer	Cure action
A) Asphaltum	1, *3, 4, *5, *6	hydrocarbon solvents	mineral oil or plasticizers	air cure by solvent evap.
B) Cellulose acetate	1, 4, *5, *6	acetone	plasticizers	air cure by solvent evap.
C) Nitrocellulose lacquer	1, 4, *5, *6	acetone	plasticizers	air cure by solvent evap.

Resin	Properties	Extender	Elastomer	Cure action
D) P-ban polymer (true composite)	1, 2, 3, 4, 5, 6	plasticizers	plasticizers	cross-links with curative
E) Poly BD R-45M resin (true composite)	1, 2, 3, 4, 5, 6	plasticizers	plasticizers	cross-links with curative
F) Polyvinyl alcohol (PVA) (water based adhesive)	1, *4,	low PVA% for low viscosity	glycerine	air cure by solvent evap.

A) Asphaltum was chosen for low cost and production ease. Although compositions using it are not "true" composites, asphalt/mineral oil mixture has many of the desirable properties of one. Early mixtures of oxidizer, asphaltum and mineral oil were used in the first composite rocket propellant. For use in smoke compositions mentioned herein, the asphaltum is dissolved in a 60/40 solvent/mineral oil mixture and the appropriate amounts of solid ingredients are mixed into it. Total asphalt percentage will range between 8% and 15% by weight. The "composite" is cured at temperatures between 70° and 90° until tackless (complete solvent evaporation).

B) As an avid pyrotechnist, I have used cellulose acetate solutions as a binder for a wide variety of pyrotechnic compositions including pressed smoke mixtures and smoke "pellets" or "candles". It is inexpensive and easy to use, it supplies good adhesive properties (especially when pressed) and excellent moisture-proofing qualities as well. It ignites and burns easily but produces no smoke of its own (an asset in other compositions). Although it can be made elastomeric by the addition of plasticizers such as DOA, DBP, DOM, etc., they seem to reduce the adhesive qualities somewhat and the composition tends to "crumble" unless enough CA is used in the solution (higher solids loadings) and enough pressure is used to form the grain. A 15-20% solids loading CA solution should not use more than 10% plasticizer in the solution. For rigid sets, CA is an excellent choice.

C) Compositions employing nitrocellulose lacquer as a binder exhibit good adhesion and weather-proofing properties but similar to CA solutions, it has limited elastomeric qualities without the addition of a plasticizer. 15% solids NC lacquer with a plasticizer retains more adhesion than CA/plasticizer binders but their uses and properties are very similar. The percentage of plasticizer should not exceed 10% of the 15% NC solution percentage by weight. Weaker NC solutions would use less plasticizer accordingly. Like CA solutions, NC binders are very desirable supplying good moisture-proofing properties without affecting the combustion rate or smoke production of the composition. Again, an excellent choice for rigid or semi-rigid sets.

D) P-ban polymer has been used to produce more composite propellants than any other polymer choice. It is the binder for the rocket propellant used in the Space Shuttle SRB's and is an excellent choice for composite smoke formulations as well as other pyrotechnic applications (Composite Color Flame Formulations / Gary Purrington, Plastic Resin Bonded Rocket Fuel Systems / G. Purrington, Experimental Composite Propellant / T. McCreary) and other formularies.

PBAN can be thinned with a plasticizer or mineral oil and it cures (cross-links) using an epoxide DER-331 from Dow Chemical or Shell 828. It requires 24 to 48 hours to cure at elevated temperatures of 125° to 145° F. The toxicity of this resin system is much lower than that of R-45 which uses Isocyanates. An excellent lower cost "true composite" polymer. Example white smoke formulation to follow;

Ingredient	**Formula**	**Weight**	**Application**
Ammonium perchlorate, 200 µm	NH_4ClO_4	33.0%	oxidizer
Zinc oxide, powder	ZnO	18.0	smoke, color
Hexachloroethane, granular	$C_{10}Cl_{12}$	13.0	smoke
Ammonium chloride	NH_4Cl	11.0	smoke
Sodium bicarbonate	$NaHCO_3$	4.0	stabilizer / CO_2
Aluminum, spherical 400 mesh	Al	2.0	fuel / combustion
Red iron oxide (ferric oxide)	Fe_2O_3	1.0	combustion catalyst
PBAN polymer	Proprietary	14.0	fuel / binder
DER-331 or Shell 828 epoxy	Proprietary	3.0	fuel / curative
Versamid 140, polyamide	Proprietary	1.0	fuel / cure ctlst

Press in place with a tapered core. Prime when cured (tackless). To make insecticidal smoke add an additional 3-4% of a concentrated insecticide. This can be absorbed in sawdust and added to the mix.

E) Polybutadiene R-45M has many applications in addition to propellants and pyrotechnics. Like PBAN, newer formulations are constantly being devised using these binder systems. It may be thinned for use if necessary with a plasticizer or mineral oil and curing takes place at room temperature (+65° F) using Isonate 143-L or Papi or at elevated temperatures of +125° using IPDI. This "true composite" polymer is chosen for its rapid cure rate and excellent polymeric values.

F) Polyvinyl Alcohol - PVA was tested and can be used for smoke formulations as well but with limited desirable qualities besides ease of use and low cost. Its water base does not allow its use in combination with reactive metals and other candidate materials such as uncoated magnesium and/or other metals (production of white oxide smoke) but works fine in compositions containing no moisture sensitive/reactive agent(s). PVA beads are placed in boiling water to make the adhesive and the viscosity is adjusted by the amount of PVA added. If an elastomeric agent is needed, glycerine works better than oils or hydrocarbon plasticizers and is mixed with the PVA adhesive solution just before mixing with the other ingredients of the composition.

SMOKE COMPOSITION FORMULAE

Now you can breathe a sigh of relief. We are now over the "how and why" and can get into the heart of the text - **useable formulations**. Do not proceed unless you have previously read and understand the literature we have presented in this text. Although workable, the formulations listed herein may require slight "tweaking" to get them to perform for you as they have for me. It is also imperative that you study material safety data sheets on the chemicals you will be working with and follow suggested safety and health information listed for each.

The formulations listed herein may be used as is or altered slightly through the use of the information covered in this text to meet specific requirements such as tactical, commercial or survival applications. Observe all safety rules listed herein and test only in approved well ventilated areas. Remember, many candidates for smoke production are harmful and/or carcinogenic. Pesticides can be harmful in a number of ways including absorption through the skin. Be aware of these dangers and avoid inhalation of *any* type of smoke.

WHITE SMOKE

		% by weight	Comments
A)	Potassium nitrate	48.0	Low hygroscopicity, does not react with moisture. Humid atmospheres will not necessarily enhance the smoke density. Requires hot priming.
	Sulfur, flour	46.0	
	Sucrose	3.0	
	Charcoal, air float	3.0	
B)	Potassium nitrate	46.0	Requires priming. Caution phosphorous! This mix uses 5% dextrine. Phosphorous is moistened with water separate from others (wet) then mixed and cast.
	Sulfur, flour	45.0	
	Lampblack	6.0	
	Red phosphorous	3.0	
	Dextrine (additional)	5.0	
C)	Hexachloroethane	44.0	Difficult to ignite, requires thermic prime. Mix is hygroscopic and produces chlorine HCl smoke. Must be sealed well/storage.
	Zinc oxide	46.0	
	Aluminum, dark pyro	6.0	
	Sucrose	4.0	
D)	Hexachloroethane	48.0	Difficult to ignite, requires thermic prime. Mix is hygroscopic and **must be sealed** well to prevent possible spontaneous combustion (contains zinc). Produces HCl smoke.
	Zinc oxide	27.0	
	Zinc dust	20.0	
	Lactose	3.0	
	Magnesium carbonate	2.0	
E)	Hexachloroethane	45.0	Same cautions as C above. In addition, this one also forms silicic acid - irritating!
	Zinc oxide	43.0	
	Calcium silicide	10.0	
	Magnesium oxide	2.0	

F)	Hexachloroethane	40.0	Hygroscopic, must be sealed well. Easier to ignite than other HCE mixes but still requires hot prime. Caution - contains chlorate (sensitive).
	Zinc oxide	40.0	
	Potassium chlorate	13.0	
	Ammonium chloride	7.0	
G)	Ammonium chloride	50.0	Contains chlorate. Increased sensitivity but good ignition using ordinary primes. Lower heat generation than other mixes.
	Potassium chlorate	30.0	
	Asphaltum	10.0	
	Zinc oxide	5.0	
	Sucrose	4.0	
	Magnesium carbonate	1.0	
H)	Ammonium chloride	48.0	Same cautions as listed for G above.
	Potassium chlorate	29.0	
	Naphthalene (moth balls)	10.0	
	Lactose	4.0	
	Zinc oxide	8.0	
	Magnesium carbonate	1.0	
I)	Hexachloroethane	39.0	Self sealing composition when enough CA solution is used to moisten completely before pressing. Requires prime.
	Ammonium perchlorate	20.0	
	Zinc oxide	33.0	
	Sucrose or dextrose	4.0	
	Cellulose acetate solution	+	

Most white smoke compositions (except A & B) form chlorides and/or oxides during combustion that rely on moisture in the air for condensation to take place forming the white cloud. Therefore, the smoke density from these compositions would be enhanced in humid climates. The smoke generated by formulations A & B is of burning sulfur which does not necessarily require moisture or condensation to form the cloud which is not as dense, heavy (staying lower to the ground) or pure in color as those that condensate.

BLACK SMOKE

		% by weight	Comments
A)	Hexachloroethane	59.0	Requires thermic prime for ignition. The magnesium must be coated prior to adding.
	*Magnesium AFA 250	13.0	
	Naphthalene (moth balls)	20.0	
	Sucrose	6.5	
	Magnesium carbonate	1.5	
B)	Potassium perchlorate	53.0	Somewhat difficult to ignite, hot prime is required. The rosin may be made into a solution with alcohol to double as the binder.
	Anthracene	32.0	
	Sulfur, flour	9.0	
	Rosin	4.5	
	Magnesium carbonate	1.5	

C)	Potassium chlorate	41.0	Caution - contains chlorate! The chlorate is mixed well into the CA solution before the other ingredients are added. If the mix is too thick, more CA solution may be added for casting.
	Antimony sulfide, 200 mesh	20.0	
	Naphthalene (moth balls)	15.0	
	Asphaltum	16.0	
	Cellulose acetate solution	8.0	
D)	Potassium chlorate	45.0	Caution - contains chlorate!
	Asphaltum	40.0	
	Charcoal, air float	10.0	
	Dextrose	3.5	
	Magnesium carbonate	1.5	

Black smoke is formed from the incomplete combustion of substances (or mixtures) containing carbon rich materials in free access to atmospheric oxygen at the burn surface. Therefore, black smoke compositions do not require confinement to produce good color. In fact, in a container with a vent, the smoke can be produced from the tip of a flame from the vent. If the color is gray, there is usually a lack of atmospheric oxygen in the reaction zone and carbonaceous materials are subliming instead of combusting to form the required black "soot" smoke. These compositions are not necessarily enhanced by moisture in the air.

COLOR DYE SMOKE COMPOSITIONS

Most of the technical information on color smoke production has been previously listed in this text. However, I feel it important to add a few notes on testing potential dye candidates for use as color donors.

In order to produce color, the dye must be vaporized by the combustion heat of the fuel(s) and exit the reaction zone attached to the by-product gasses where it condenses in air to re-form the vapors once again into *solid* dye particles we view as color smoke. Moisture *does* play a big role here. The more moisture (humidity) in the air, the higher the density of the smoke and the richer the color. It is the *moisture* that changes the dye vapors back into solid particles and the more moisture there is, the faster this takes place tending to agglomerate the particles together as density.

The process involves heating the dye to a sufficient temperature causing vaporization of the dye molecules with a minimum of heat. If too much heat is generated, the dye is decomposed with the fuel(s) and poor or no color will result. This reason alone warrants the use of a dye that has a decomposition temperature *higher* that its melting point. The larger the difference between the two, the better the dye will work for color smoke applications. Most pigments and dyes have decomposition points lower than their theoretical melting points. These cannot be used to produce color smoke. If they don't melt before they decompose, they are useless as color smoke candidates. Useable dyes must meet the following criteria;

1) Must volatilize rapidly at temperatures well below 500° C with a minimum of decomposition (typically less than 20%). *The lower the melting point, the faster this will happen and with a very minimum of loss by combustion.*

2) Smoke formed should condense into distinct, specific color as per the dye sample and should remain stable until dispersed by the air (diluted). *Distinct, rich color should ensue directly from the reaction surface only to be diluted in the air well afterward as weaker color.*

3) The dye candidate must be of a concentration to produce rich color when a minimum of 30% is used in the formulation. *Many smoke formulations call for up to 50% dye but the average will range at about 40%. The dye is a diluent. The larger its percentage in the formulation, the slower the combustion rate. If it burns too slow, the volume of smoke produced per second is decreased along with the color quality.*

The procedure for testing smoke dye candidates is simple. The first step is to study the technical information for the sample as supplied by the manufacturer. The information you will need is carcinogenity (preferably not), melting point and decomposition point. This information is not usually supplied with the MSDS and therefore you must ask for it. If surplus dyes are used and no information is available, they may be tested in the following manner;

Heat a crucible or a tin plate over a burner and drop a very tiny pinch of dye onto it. If the dye decomposes with no color vapors, it will not work as a smoke dye. If the color is poor and/or very little of it, check the surface of the heated crucible with a candy thermometer or similar making sure the temperature is *less* than 500 °C (932 °F). If the heat was higher than this, reduce the temperature a bit and test the dye again. If poor color still results, the dye is a poor candidate for use and would require too much dye in the formulation to be useful. If it melts rapidly and vaporizes with color, it can be added to your list as a smoke dye candidate for further testing.

Color is largely determined by reflected light. Because of this, the experiment should be conducted in sunlight with proper ventilation. Shaded areas or poor light conditions will result in darker, less vivid color. The following is a list of dye chemical groups we have tested with success;

Anthraquinone
Azo derivatives
Diphenylmethane (auramine 00)
Ketone Imine (auramine 0)
Perinone
Rosindone
Solvent dyes
Thiazine (methylene blue)
Triphenylmethane (basic green)
Xanthene (rhodamine B)

For safety sake, choose candidates of low toxicity and low or no carcinogenic traits.

VIOLET / RASPBERRY

		% by weight	Purpose
A)	Rhodamine B (Xanthene)	48.0	dye (color)
	Potassium chlorate	26.0	oxidizer
	Lactose	15.0	fuel / smoke / gas
	Cellulose (ground wood or paper)	6.0	fuel / ash quality
	Magnesium carbonate	5.0	stabilizer / coolant / gas

Comments; Raspberry / violet in coloration - very rich, bright color. Caution - Rhodamine B stains everything it comes in contact with and is difficult to remove. Cover all surfaces and wear rubber gloves.

B)	Rhodamine B (Xanthene)	41.0	dye / color
	Sodium nitrate	27.0	oxidizer
	Cellulose	27.0	fuel / ash quality
	Sucrose	3.0	fuel / smoke / gas
	Magnesium carbonate	2.0	stabilizer / coolant / gas

Comments; Hygroscopic, requires moisture-proof sealer. Slightly more difficult to ignite but not as sensitive as chlorate compositions to work with. Can be used to make smoke stars in combination with black powder bursts.

C)	Methylene blue (Thiazine)	4.0	dye / color
	Rhodamine B (Xanthene)	43.0	dye / color
	Potassium chlorate	26.0	oxidizer
	Sucrose	14.0	fuel / smoke / gas
	Cellulose	8.0	fuel / ash quality
	Zinc oxide	5.0	stabilizer / coolant / smoke

Comments; Deeper coloration than the above formulations (more blue). The more blue dye added, the closer to violet in color.

Additional comments; Cellulose is added in an effort to reduce ash density by providing a more porous ash column for dye vapor release. Cellulose combusts easily with a minimum of ash. This increases porosity which opens more "avenues" for the vapors to exit the developing ash column. With less dye vapors being "filtered" out by the ash, the more rich the color of smoke will be.

BLUE

A)	Indigo, synthetic	20.0	dye / color
	Blue (Thiazine)	30.0	dye / color
	Potassium chlorate	26.0	oxidizer
	Sucrose	14.0	fuel / smoke / gas
	Cellulose (ground wood or paper)	7.0	fuel / ash quality
	Magnesium carbonate	3.0	stabilizer / coolant / gas

Comments; Requires higher than normal combustion temperatures for best color. Oxidizer can be increased if it is required for good color (slight increase only).

B)	Blue (Anthraquinone)	45.0	dye / color
	Potassium chlorate	25.0	oxidizer
	Sucrose	15.0	fuel / smoke / gas
	Cellulose	10.0	fuel / ash quality
	Magnesium carbonate	5.0	stabilizer / coolant / gas

Comments; Richer blue color at a wide range of combustion temperatures.

C)	Blue (Anthraquinone)	40.0	dye / color
	Potassium chlorate	26.0	oxidizer
	Sulfur, flour	10.0	fuel / smoke
	Sodium bicarbonate	24.0	stabilizer / coolant / ash qlty

Comments; Rich, deep color. High $NaHCO_3$ reduces sensitive nature of S / $KClO_3$ combination.

D)	Blue (Anthraquinone)	38.0	dye / color
	Guanidine nitrate	35.0	oxidizer
	Cellulose	16.0	fuel / ash quality
	Sucrose	8.0	fuel / smoke / gas
	Magnesium carbonate	3.0	stabilizer / coolant / gas

Comments; Lower combustion temperatures with good color.

GREEN

A)	Blue (Anthraquinone dye)	12.0	dye / color
	Yellow (Diphenylmethane)	28.0	dye / color
	Potassium chlorate	26.0	oxidizer
	Sulfur, flour	10.0	fuel / smoke / gas
	Sodium bicarbonate	24.0	stabilizer / coolant / ash qlty

Comments; Rich green color. Dye ratios can be adjusted to obtain color depth from forest green to lime green.

B)	Green (Anthraquinone)	42.0	dye / color
	Potassium chlorate	26.0	oxidizer
	Sulfur, flour	9.0	fuel / smoke / gas
	Sodium bicarbonate	23.0	stabilizer / coolant / ash qlty

Comments; Good rich emerald green color.

C)	Green (Anthraquinone)	47.0	dye / color
	Potassium chlorate	27.0	oxidizer
	Sucrose	10.0	fuel / smoke / gas
	Cellulose	11.0	fuel / ash quality
	Zinc oxide	5.0	stabilizer / coolant / smoke

Comments; Good rich smoke color and density.

D)	Green (solvent dye)	40.0	dye / color
	Potassium perchlorate	29.0	oxidizer
	Antimony sulfide 200 mesh	20.0	fuel / combustion / smoke
	Cellulose	8.0	fuel / ash quality
	Magnesium carbonate	3.0	stabilizer / coolant / gas

Comments; No chlorate. Less sensitive with good color and burn.

RED

A)	Red (Mono azo or anthraquinone)	45.0	dye / color
	Potassium chlorate	25.0	oxidizer
	Lactose	15.0	fuel / smoke / gas
	Cellulose	10.0	fuel / ash quality
	Magnesium carbonate	5.0	stabilizer / coolant / gas

Comments; Good color and smoke volume. Easily ignited with smooth burn.

B)	Red / orange (Mono azo)	35.0	dye / color
	Rhodamine B (Xanthene)	10.0	dye / color
	Potassium chlorate	27.0	oxidizer
	Sucrose	20.0	fuel / smoke / gas
	Zinc oxide	8.0	stabilizer / coolant / smoke

Comments; Larger ash development. Best used in open top smoke "pots". Deep rich color with volumes of dense smoke.

C)	Paranitraniline red (Aniline dye)	48.0	dye / color
	Potassium chlorate	27.0	oxidizer
	Lactose	19.0	fuel / smoke / gas
	Magnesium carbonate	6.0	stabilizer / coolant / gas

Comments; Deep rich blood red color, easily ignited with smooth burn.

ORANGE

A)	Chrysoidine (Mono azo)	49.0	dye / color
	Potassium chlorate	27.0	oxidizer
	Sucrose	12.0	fuel / smoke / gas
	Cellulose	8.0	fuel / ash quality
	Magnesium carbonate	4.0	stabilizer / coolant / gas

Comments; Good orange color and smoke volume.

B)	Oil scarlet (Mono azo)	47.0	dye / color
	Potassium chlorate	26.0	oxidizer
	Sucrose	19.0	fuel / smoke / gas
	Magnesium carbonate	8.0	stabilizer / coolant / gas

Comments; Mono azo dye appears to produce good, deep color even at higher combustion temperatures that would decompose some other dye candidates.

C)	Oil scarlet (Mono azo)	38.0	dye / color
	Auramine O (Diphenylmethane)	9.0	dye / color
	Potassium chlorate	26.0	oxidizer
	Sucrose	17.0	fuel / smoke / gas
	Cellulose	5.0	fuel / ash quality
	Magnesium carbonate	5.0	stabilizer / coolant / gas

Comments; Brighter in color, not as deep, not as "brown" as "B" above. Excellent volume and color.

YELLOW

A)	Auramine O (Diphenylmethane)	45.0	dye / color
	Potassium chlorate	26.0	oxidizer
	Sucrose	16.0	fuel / smoke / gas
	Cellulose	8.0	fuel / ash quality
	Magnesium carbonate	5.0	stabilizer / coolant / gas

Comments; Excellent canary yellow color with a hint of green.

B)	Chrysoidine (Mono azo)	8.0	dye / color
	Auramine O (Diphenylmethane)	37.0	dye / color
	Potassium chlorate	28.0	oxidizer
	Lactose	22.0	fuel / smoke / gas
	Magnesium carbonate	5.0	stabilizer / coolant / gas

Comments; Bright canary yellow smoke - excellent coloration.

C)	Auramine O (Diphenylmethane)	40.0	dye / color
	Potassium chlorate	25.0	oxidizer
	Sulfur, flour	10.0	fuel / smoke / gas
	Sodium bicarbonate	25.0	stabilizer / coolant / ash qlty

Comments; Military type formulation. Good color and volume.

HINTS ON PRODUCING CUSTOM COLORS

Producing different shades or custom colors is possible simply by mixing the appropriate color dyes together. To reduce your research time, we offer the following information;

To mix for custom colors, candidate dyes should have approximately the same melting and decomposition points of one another. Usually, if the dyes you have chosen will work to produce color smoke by themselves, they will work in combination to produce the custom color as well. On the other hand, diluting a red dye with white to produce pink will not work in most cases. Do you know why? It has been covered in this text. Yes, that's correct......the white smoke compositions burn too hot and will most likely destroy the dye before it vaporizes from the reaction zone. Instead, use less red dye to weaken the color thus producing a pink in various depths according to the dye percentage used. However, pink is not a color I would produce so I list it only for the object lesson. The same reasoning applies to making powder blue from dark blue dyes.

Dyes of the same chemical family will usually have similar melting points and would be the obvious choice in combination to produce custom colors. However, if dyes of the same chemical family are not available, go back to the crucible burn test.

Mix the appropriate amount of dye(s) together with enough solvent to make a paste. Allow to dry and drop a bit onto the hot plate or crucible and note the results as previously explained. Mixing with solvent disperses the two dyes evenly together which allows the two to vaporize together which will yield the best color. We have found this to be the best process over mixing and burn testing the dyes in powder form. Once you arrive at the proper ratio, the next step is to test it in formulation. Here, the dyes are added to enough solvent to make a *runny* paste then the other ingredients are added and mixed until well homogenized. The solvent should be evaporated at this point. Be sure you record all your efforts for future use. Remember, dyes ***stain!***

I hope you have enjoyed this text as much as I did performing the tests for it. Thanks.
Gary W. Purrington - Text upgrade finished December 2000