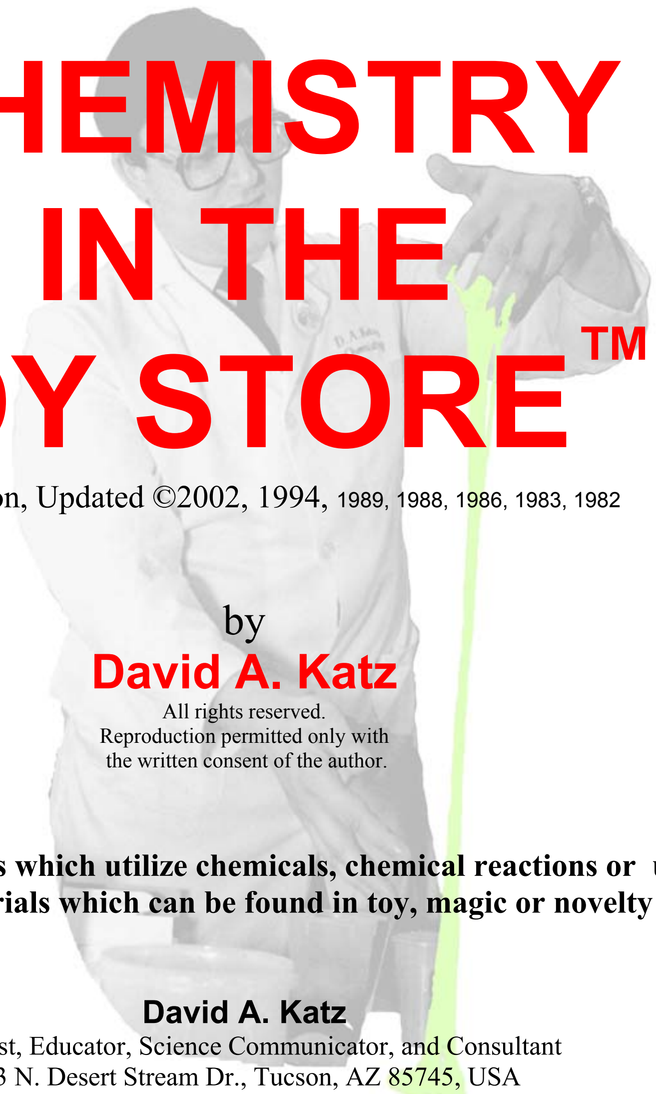


CHEMISTRY IN THE TOY STORE™

by

David A. Katz

A look at some toys which utilize chemicals, chemical reactions or unique properties of materials which can be found in toy, magic or novelty stores.

David A. Katz
Chemist, Educator, Science Communicator, and Consultant
133 N. Desert Stream Dr., Tucson, AZ 85745, USA
Voice/Fax/Message: 520-624-2207 Email: dakatz45@msn.com

PART III: Lightsticks, Magic Sand, Magic Rocks, Liquid Crystals, Dissolving Paper, Disappearing Ink, Flammables, and Big Bang Cannons

LIGHTSTICKS

CYALUME® lightsticks, manufactured by American Cyanamid Co., with similar items available from other manufacturers, are devices that produce a "cool-light" by means of a chemical reaction. The reaction is similar to the one that produces light in a firefly, but the chemicals involved are different.

A lightstick consists of dilute hydrogen peroxide solution in a phthalic ester solvent contained in a thin glass ampoule which is surrounded by a solution containing a phenyl oxalate ester and the fluorescent dye 9,10-bis(phenylethynyl)anthracene, (blue lightsticks use 9,10-diphenylanthracene) all contained in a plastic tubular container. When the glass ampoule is broken, by bending the lightstick, the hydrogen peroxide and the phenyl oxalate ester react to form phenol and some intermediate (short lived) compounds. During the reaction, the energy given off is transferred to the dye molecules. The excited dye molecules (designated as Dye®) give off the excess energy in the form of light without any noticeable heat. Thus the name, "cool-light".

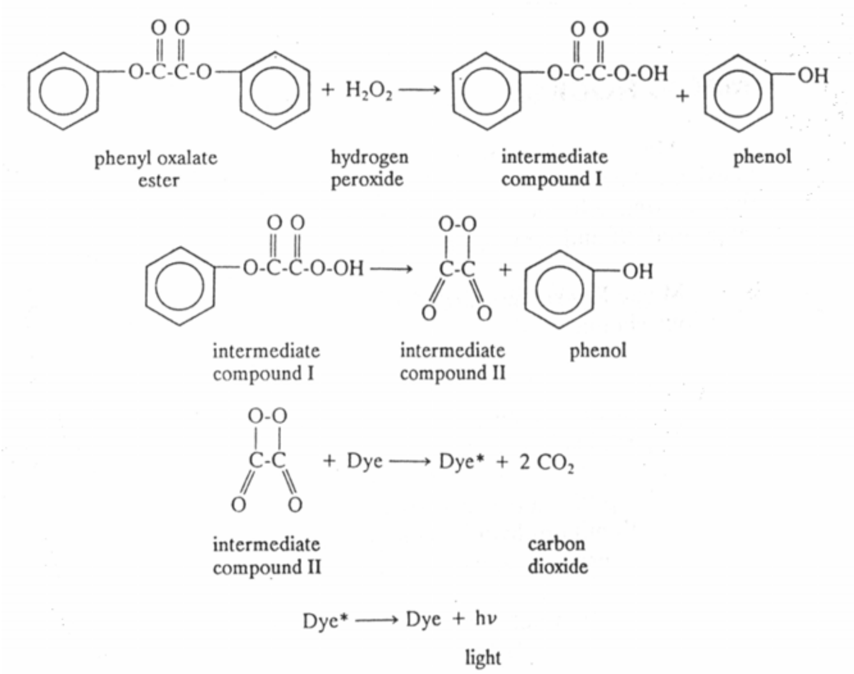


Figure 20. Summary of the lightstick reaction (from Shakhashiri, *Chemical Demonstrations*, Vol. 1, Univ. Wisconsin Press, 1983)

Lightsticks can be used to demonstrate how the rate of a chemical reaction varies with temperature. To do this, initiate three lightsticks. Place one lightstic in ice water, one in hot tap water (not boiling), and leave one at room temperature as a control. The effect of temperature on the reaction can be observed within a few minutes.

Lightsticks are used as emergency lights and safety lights in industry and for camping. As toys, they are made in the form of earrings, necklaces, bracelets, rings, eyeglasses, and bowties. They are also used to light up balls, golf balls, and flying disks for nighttime playing.

A recent variation of lightsticks are Magic in the Night® light shapes. These are adhesive backed packets in various shapes, such as circles, diamonds, and stars, and filled with lightstick chemicals which are stored in separate glass ampoules. Both ampoules must be broken in order to mix the chemicals.

Lightsticks are dated to indicate their life time. If stored in a cool place, they remain active for at least one year past that date. Light shapes have no expiration date.

MAGIC SAND®

Magic Sand®, also called Super Sand™ and Mystic Sand, is sand (silicon dioxide) that has been treated with a colored dye and coated with a finely divided hydrophobic silicon coating. Due to its hydrophobic coating, Magic Sand® can be placed in water to form underwater towers or columns and designs, and then be removed and found to be completely dry. Because of its water repellency, the particles of Magic Sand® will stay together as a separate phase in the water similar to the phase separation of a polar and a non-polar liquid such as vinegar and oil

The Magic Sand® is an application of an invention from Cabot Corporation, Boston, Mass, originally used for the removal of oily contaminants from water systems. A similar material is a fumed silicon dioxide, called Cab-O-Sil, marketed by Cabot Corp. which is used for many applications such as thickening, thixotropy, suspension of solids, and optical clarity in products such as coatings, adhesives, cosmetics, inks, plastics, and rubbers. It is also used as an anti-caking agent to promote the free flow of dry powders.

Magic Sand® is prepared by treating an inland sand (which has grains with rounded edges for better flow characteristics) with an organohalosilane such as dimethyldichlorosilane, $(CH_3)_2SiCl_2$. In the reaction, the surface of the sand becomes coated with a thin monolayer silicone film, $(CH_3)_2(OH)Si\text{-}O\text{-}$ which repels water because it is similar to a hydrocarbon film. Materials such as paper, wood, glass, silk, and porcelain can also be coated with a water-repellent film by simply exposing them to the vapor of organohalosilanes.

A Magic Sand® type of material can be made by spraying oven dried sand (one hour at 250°F) with a water-repellent material such as Scotch-gard®.

MAGIC ROCKS®

Magic Rocks®, manufactured by Magic Rocks and Craft House Corporation, are also known as a "Chemical Garden". They consist of small "rocks" colored white, blue, green, red, purple, and orange or yellow. When placed in the "growing solution", the rocks grow forming colored columns. After growth is complete, the growing solution can be poured off and replaced by water so that the Magic Rock garden can be maintained for decoration.

Magic Rocks® consist of a sodium silicate solution in water, Na_2SiO_3, (the growing solution) and small chunks of various chemical salts. Some commonly used salts and their colors are:

> calcium chloride (white), copper(II) sulfate (blue), cobalt(II) chloride (red), iron(III) chloride (yellow or orange), nickel(II) nitrate (green), and manganese(II) chloride (pink or purple). In the past, lead(II) nitrate was used as for white crystals.

To keep the salts stable (some of these are deliquescent or slightly efflorescent), they seem to be dispersed in an alum or aluminum hydroxide and thus do not crumble easily. Attempting to dissolve the colored "rocks" in water or dilute acid results in a gelatinous precipitate.

The reaction between the salt that composes the Rock and the sodium silicate results in the formation of a gelatinous precipitate that forms a barrier between the reactants. This film then develops cracks and, since it is not firmly adhered to the salt, allows further contact between the reactants. The mobile reactant (the salt) penetrates between the precipitate and the support and a new layer of precipitate displaces the first. New precipitate may be formed wherever a crack appears and the shape of the precipitate may be anything from a roughly symmetrical, cauliflower-like growth to long, slender shoots or thin, serrated sheets.

The fact that the "rocks" are composed of highly soluble salts with a high rate of solution result in rapid growth of precipitate. The cracks in the gelatinous layer is caused by a large difference in osmotic pressure between the silicate growing medium and the saturated salt solution. The sodium silicate does not have a high osmotic pressure even when concentrated because much of the silica present is in the form of aggregates (colloidal micelles or giant ions) so that the ionic strength is quite low.

If one observes the slender shoots formed in the first stages of growth, they will see and air bubble leading the growth upward in a jerky, side to side type of motion. This is often cited as evidence that a gelatinous membrane bursts periodically and a new precipitate forms.

To make a chemical garden, mix 100 mL of sodium silicate solution (available from chemical supply companies and some hobby shops) with 400 mL of water in a 600-mL beaker or glass. Add sufficient sand (silicon dioxide) to form a thin layer on the bottom of the container and allow it to settle. Add crystals or chunks of any of the above salts to the solution, but do not add too many at one time to prevent cloudy solutions and heavy precipitates. After the garden is grown, it can be saved by siphoning off the sodium silicate solution and replacing it with water.

MAGIC TREE®

Magic Tree® is a miniature artificial tree that grows forming ornamental "buds" in as little as 15 minutes, and "magically" growing into a delicate tree in about 2 hours. Magic Tree® is manufactured by New Tomorrow, Inc.

A Magic Tree® consists of two pieces of green or white colored blotter paper cut so as to be assembled into a small evergreen tree with spots of dye on the ends of the branch tips. The tree is placed in a solution made by mixing a small packet of blue powder with 1 teaspoon of water and, over a period of time, small crystals will grow on the ends of the branches. After about 2 hours, the ends of the branches contain clusters of crystals. The tree can be dried and, if protected, can last for months.

The dyes on the Magic Tree® are mainly water soluble food colors. The growing solution is made from an alkaline salt, ammonia, and water. A representative solution can be made from 6 tbsp sodium chloride (this is not an alkaline salt), 1 tbsp ammonia, 6 tbsp water, and 6 tbsp liquid laundry bluing. In operation, the solution moves up the tree by capillary action. The tree is permeated by the solution, however, the branch tips, being tapered to a point, experience the most rapid rate of evaporation resulting in crystal formation.

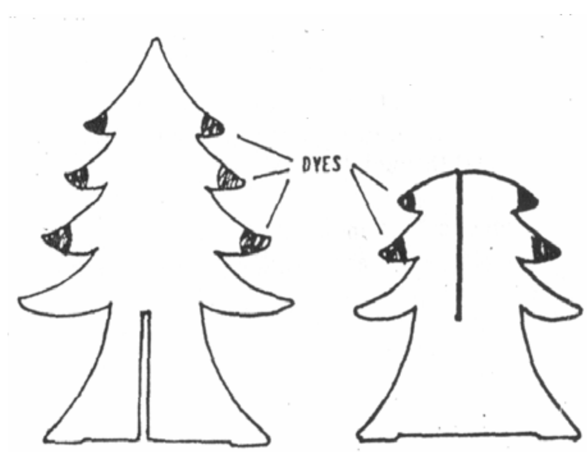


Figure 21. An unassembled Magic Tree®

Laundry bluing, used to whiten fabrics which have turned yellow or gray, is composed of a colloidal solution of Prussian blue which is used as a blue pigment that makes fabrics appear white. Prussian blue is made by reacting potassium ferrocyanide with iron(III) sulfate:

$$3\ K_4Fe(CN)_6 + 2\ Fe_2(SO_4)_3 + x\ H_2O \rightarrow Fe_4[Fe(CN)_6]_3\ xH_2O + 6\ K_2SO_4$$

Note: x = 14-16

Prussian blue is formed as a precipitate (it is not soluble in water). This reaction, however, is the ideal case when the reaction occurs very slowly. If formed quickly, as is usually the case, the Prussian blue is more likely to have the formula $K[Fe^{II}Fe^{III}(CN)_6]\ xH_2O$. It contains iron in both the +2 and +3 oxidation states, as denoted by the Roman numerals. The intense color is due to charge-transfer from Fe^{II} to Fe^{III}. (There is no color if both iron atoms are in the same oxidation state.)

Figure 22. Assembled Magic Tree® in growing solution.

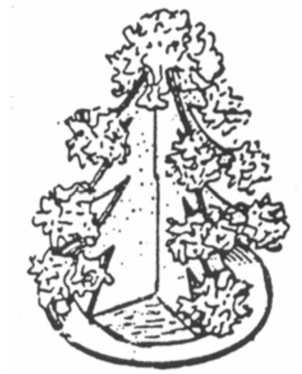


Figure 23. Magic Tree® showing crystal growth.

Addition of ammonia, a base, and salt does not change the color of the bluing solution, but the crystals that grow are white. It is suspected that during the evaporation of solvent and resulting crystallization there is probably a reduction of the Prussian blue forming white $K_2Fe^{II}Fe^{II}(CN)_6$ where additional K^+ ions would fill in the crystal lattice due to the openings left by reduction of Fe^{III} to Fe^{II}. Since there are few additional potassium ions in solution, the lattice is probably filled by the Na^+ ions from the salt forming $KNaFe^{II}Fe^{II}(CN)_6$) which should also be white in color. The potassium compound, $K_2Fe^{II}Fe^{II}(CN)_6$, is known as Everitt's salt (first reported by Thomas Everitt is 1835 by boiling potassium ferrocyanide with dilute sulfuric acid).

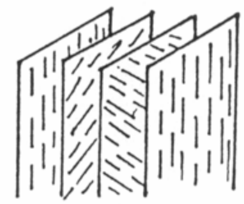
LIQUID CRYSTALS

Liquid crystals are organic compounds that are in a state between liquid and solid forms. They are viscous, jelly-like materials that resemble liquids in certain respects (viscosity) and crystals in other properties (light scattering and reflection). Liquid crystals must be geometrically highly anisotropic (having different optical properties in different directions)-usually long and narrow - and revert to an isotropic liquid (same optical properties in all directions) through thermal action (heat) or by the influence of a solvent. Liquid crystals are classified as:

smectic: molecules arranged in horizontal layers or strata and are standing on end either vertically or at a tilt.

nematic: molecules possess a high degree of long-range order with their long axes approximately parallel, but without the distinct layers of the smectic crystals.

lyotropic: molecules consist of a nonpolar hydrocarbon chain with a polar head group. In a solvent, such as water, the water molecules are sandwiched between the polar heads of adjacent layers while the hydrocarbon tails lie in a nonpolar environment.



If smectic and nematic liquid crystals are subjected to changes in temperature, they change their form and their light transmission properties splitting a beam of ordinary light into two polarized components to produce the phenomenon of double refraction. This results in the appearance of the characteristic iridescent colors of these types of liquid crystals. This type of liquid crystal finds use in thermometers, egg timers, and other heat sensing devices. Changes in structure can also be accomplished using a magnetic field which make them useful in calculator or other LCD displays. Temperature sensitive liquid crystals were used in Mood Rings.

When lyotropic liquid crystals are subjected to disturbances, such as stirring or squeezing, the layers of crystals are disturbed altering their light transmission characteristics to produce color changes similar to the smectic and nematic liquid crystals described above. These are the type of liquid crystals used in the Press Me stickers.

Some liquid crystal products are: Mood Rings; Liquid crystal stickers, called Press Me stickers, which come in various shapes and swirl into many different colors when gentle pressure is applied; A plastic disc called a Space Fidgit®, made by A.R.C., contains mixture of temperature and pressure sensitive liquid crystal material which exhibits color patterns when rubbing its back or changing its temperature; and Fickle Foam, made by Davis Liquid Crystals, which is temperature sensitive liquid crystal sheet mounted on a thin foam pad.

Another application of liquid crystals is in Hot Wheels Color Racers® and Color FX™ cars manufactured by Mattel Toy Corp. These are model cars that are painted with a temperature sensitive liquid crystal paint and which change colors when placed in icy cold or warm tap water.

Other novel applications of liquid crystal materials are in Mattel's Nickelodeon™ Color Writer™ Drawing Screen, in dolls such as Lil Miss Magic Hair™, Hollywood Hair™ Ken , and Secret Hearts™ Barbie , and in Playskool's Magic Lemonade Party™ or Magic Breakfast Party™. In the Nickeloden™ Color Writer™, a heat pen, powered by two batteries, is used to write or draw on a black liquid crystal screen. When warmed, the liquid crystals become transparent and the colors of the board behind the liquid crystals in visible. To erase the drawing, an ice cube is used, in a metal eraser container. In the dolls, hair or clothing is impregnated with liquid crystal material. Depending on the doll, warming or cooling using a wand or plastic bag filled with water will cause hair color to change, or stars or hearts to appear in hair or clothing. The Magic Lemonade or Breakfast Party, and similar toys, use liquid crystal material to make pitchers, knives, cookies, and muffins change color to simulate pink lemonade, orange juice, and jelly on toast or muffins. In summary, whenever a substance or object changes color with a change in temperature, it is a high probability that liquid crystals are involved.

MELTING MONEY AND MAGIC NURSERY™ TOYS

Melting Money and Melting Memos, which were marketed by So Much Fun!, are paper items that dissolve when placed in water. The paper is composed of carboxymethylcellulose (starch) with 20% or less cellulose (wood fibers). This material has been used by organizations such as the CIA for secret or sensitive documents which can easily be destroyed by wetting with water.

A number of toys using dissolving paper have appeared. Trash Bag Bunch™, from Lewis Galoob Toys, consist of plastic figures contained in a dissolving paper garbage bag. When placed in warm water, the garbage bag dissolves and the figure is obtained. A variation of this is Mattel's Hot Wheels Revealers, Hot Wheels cars wrapped in a dissolving paper cover.

A novel use of dissolving paper is the Magic Nursery™ toys. Magic Nursery™ dolls are packaged in dissolving paper clothes and had to be placed in water to discover if the doll was a boy or a girl. There are also a number of Magic Nursery™ accessories, one of which are Bye-Bye Diapers™. These paper diapers fit Magic Nursery and other 10-inch to 14-inch dolls. Instead of disposing of the diapers after play, they are placed in water and dissolve to leave a plastic package containing a pair of cloth training pants with the words "I'm in training" printed on them.

Currently, dissolving paper is available from Flinn Scientific as melting mole dollars.

SMELLY PATCHES AND SCRATCH AND SNIFF STICKERS

Smelly Patches are cloth patches backed with a heat activated adhesive that can be applied to clothing or other objects. Smelly Patches contain a picture of a fruit such as apples, grapes, strawberries, etc..., and also smell like the fruit that is pictured. The smell is a result of natural fragrances or esters that are microencapsulated onto the surface of the Smelly Patch.

Microencapsulation is a process where substances such as inks or dyes, adhesives, cosmetics, pharmaceuticals, or fragrances are contained in microscopic capsules, 20 to 150 microns in diameter, which can be broken mechanically, electrically, or chemically to release the contents. The microcapsules are composed of different materials depending on the substance packaged and the method by which it is to be released. Gelatin is widely used as an encapsulating agent. The advantage of microencapsulation is that the capsules remain stable and inert until broken down. A major producer of microencapsulated materials is the 3M Corporation.

A similar product to the Smelly Patches are scratch and sniff spots which are often used in magazine or direct mail advertisements or children's books. There are also scratch and sniff stickers. In both cases, an individual usually uses a fingernail to mechanically break the microcapsules releasing the contents.

Flavors and fragrances may utilize a single ester or a mixture of esters and other substances. Some esters that smell like common materials that can be prepared in the laboratory are listed in Table 1.

Table 1. Common esters used for flavors and fragrances

Ester	Smells like	Prepared from
isoamyl acetate	banana	isoamyl alcohol and acetic acid
ethyl butyrate	pineapple	ethanol and butanoic acid
benzyl acetate	peaches	benzyl alcohol and acetic acid
n-propyl acetate	pears	n-propyl alcohol and acetic acid
benzyl butyrate	flowers	benzyl alcohol and butanoic acid
methyl butyrate	apples	methanol and butanoic acid
isobutyl propionate	rum	isobutyl alcohol and propionic acid
octyl acetate	oranges	octanol and acetic acid
methyl anthranilate	grapes	methanol and 2-aminobenzoic acid

Esters can be made, in the laboratory, by mixing a few mL each of an alcohol and an organic acid and adding a few drops of concentrated sulfuric acid or phosphoric acid. The acid should generate sufficient heat to initiate the reaction, but the mixture can be heated in a water bath if necessary. If the esters are intended to be passed around a group of people, add a small amount of glass wool to the container to prevent spilling or splashing.

NITINOL: THERMOBILES AND BUTTERFLIES

Nitinol is a nickel-titanium alloy that was first made at the U.S. Naval Ordnance Laboratory. This alloy exhibits a shape memory effect, that is, it radically changes shape when subjected to a temperature change. Nitinol wire is soft at a low temperature and can easily be bent into simple shapes. At high temperature. the Nitinol wire becomes stiff reverting to its original shape.

One application of Nitinol is the Thermobile (see Figure 24), a device consisting of a wire loop around two pulleys, one brass and one plastic, that generates power without a motor or batteries. The Thermobile is manufactured by Innovative Technology International, Inc.

The Thermobile works by immersing the bottom edge of the brass pulley into hot water between 50°C and 75°C. Within a few seconds, the Thermobile will begin to spin continuing as long as the bottom is at a temperature above 50°C. What takes place is that the Nitinol wire, bent around the metal pulley, will try to straighten itself out and, in the process, will cause the wheel to spin. The effect can also be produced by using solar energy, with the aid of a magnifying glass, to heat the brass pulley.

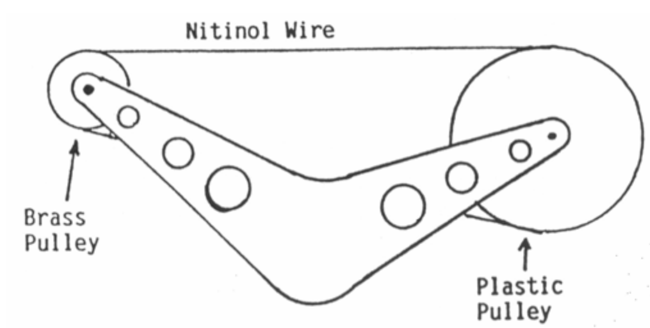


Figure 24. A Thermobile

An improved version of Nitinol wire, consisting of approximately 50% each of nickel and titanium is manufactured by Toki Corporation under the name BioMetal®. This alloy has been stretched and, when heated, will shorten to its original shape. BioMetal® wire is used in a device called Space Wings and a Kinetic Butterfly, butterfly types of devices which flaps their wings due to the contraction of the BioMetal® wire.

DISAPPEARING INK

Disappearing ink is a bright blue water-based solution which, when squirted on clothing, table cloths, or other materials, will disappear within minutes leaving only a colorless "water spot" that will evaporate slowly. When dry, there is a small amount of white residue that remains.

The pH of the disappearing ink solution is about 10-11 (moderate to strong base). Addition of acid, such as hydrochloric acid, HCl, causes the solution to turn colorless forming a white precipitate. Addition of base, such as sodium hydroxide, NaOH, dissolves the precipitate and restores the blue color. If the "ink" is squirted on cloth, the colorless water spot that remains after the color fades is slightly acidic with a pH of about 5-6. Addition of base to the water spot causes the blue color to return. The blue color is also obtained if base is placed on the dried "ink" spot.

Due to its color change with pH, the material used to make the disappearing ink was identified as an acid-base indicator called thymolphthalein, $C_{28}H_{30}O_4$ (colorless to blue at pH 9.3-10.5). This was confirmed by infrared spectrophotographic analysis by the author.

The disappearing ink is made by dissolving a small amount of thymolphthalein in ethyl alcohol followed by dilution with water. The blue color is obtained by the addition of a small quantity of sodium hydroxide solution. A red disappearing ink can be made using phenolphthalein in place of the thymolphthalein.

The pH change which causes the color to fade is a result of the reaction of the sodium hydroxide, NaOH, with carbon dioxide, CO_2, in the air to form sodium carbonate, Na_2CO_3, according to the following reaction:

$$2\,NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

Once the sodium hydroxide is neutralized, the acidity of the alcohol changes the "ink" to colorless.

Disappearing ink, both blue and red, are used as the fuel in Zap-it® guns. These are battery powered water pistols used to shoot the colored liquid which acts as an indicator to show a victim is "shot".

A novel application of the disappearing ink reaction is Mattel's Hollywood Hair™ Barbie dolls. The extra long hair of the doll is coated with phenolphthalein indicator. When sprayed with Magic Hair Mist, consisting of ethyl alcohol, water, and a base, such as sodium hydroxide, the hair of the doll turns pink. As the hair dries the pink color fades to colorless.

MYSTIC SMOKE

Mystic Smoke is a grease-like paste that produces puffs of "smoke" from the fingertips when they are squeezed together and then snapped apart. It is used by magicians or jokesters to pinch some smoke from a cigarette (either lighted or unlit) and throw it away, or to pull out "cobwebs" from an old book or their wallet.

Mystic Smoke is a grease-like paste made from a mixture of machine oil, linseed oil, scale wax, carnauba wax, soap, latex, resins, and rosin. In use, a small amount is rubbed onto the thumb and first finger of a warm hand until it is undetectable. The fingers are squeezed together, allowing the Mystic Smoke material to adhere to itself, and then snapped apart producing spider web-type strings that give the appearance of smoke

Several types of heavy greases and petroleum jelly (Vaseline) were tried by the author in an attempt to duplicate the Mystic Smoke effect without success.

SPARKLERS

Sparklers in gold, red, green, and blue colors are often used to decorate birthday cakes or similar items for parties, or for celebrating holidays. Sparklers consist of a metal wire with about 3/4 of it covered with a silver or colored hard material. The combustible material is most commonly a gunpowder type material consisting of sodium and/or potassium nitrates (chlorates may be used) with sulfur and carbon. The sparks are provided by powdered metals such as iron, aluminum, or magnesium. The metal powder is coated with paraffin wax to prevent oxidation during storage and to allow the metal to fall off the sparkler as it burns producing the characteristic sparks. Colors are produced by adding nitrate or chloride salts of strontium (red), barium (green) and copper (blue). The combination of added metal salts and paraffin wax are responsible for making the sparkler difficult to ignite. When using sparklers, take care to keep them away from the face and body, as well as away from any flammable material. After combustion is complete, the wire will be hot.

FLASH PAPER

Flash Paper is available in magicians' supply store and novelty shops. It can be purchased in pads of 20 2{ in. x 3 in. sheets (6.3 cm x 7.6 cm) and in 8 in. x 10 in. sheets (20 cm x 25 cm). It is also available in the form of Flash Bills, which approximate the size and color of a U.S. one dollar bill, and Flash Cotton.

Flash paper is commonly use by magicians to throw fire into the air or with magic wands that shoot bursts of flame. Flash paper burns leaving almost no ash.

Flash paper is nitrocellulose, sometimes called guncotton (approx. formula $C_6H_7O_2(ONO_2)_3$). It is prepared by treating cellulose, in the form of paper or cotton, with a mixture of nitric and sulfuric acids. There are many - different forms of nitrocellulose obtained by varying the strength of acids used, temperature and time of reaction, and the acid/cellulose ratio. Other uses of nitrocellulose are in fast drying automobile lacquers, collodion, rocket propellant, medicine, printing ink base, coating bookbinding cloth, and leather finishing. Nitrocellulose, as used in flash paper, is extremely flammable and some forms can explode on sharp impact.

FLASH POWDER

Flash powder can be obtained at magicians' supply stores in two different forms. One type is a pre-mixed powder, and the second type is a photographic flash powder that comes packaged in two separate containers. In practice, flash powder is used in the theater for special effects, usually with a special flash pot, when making persons or things disappear.

The pre-mixed flash powder was analyzed by the author and found to be mainly a gunpowder or black powder consisting of sodium and potassium chlorates and/or nitrates with sulfur and carbon.

The two component photographic flash powder it the type that was often used before the invention of flash bulbs. Its use can sometimes be observed in some silent movies and early talking movies. The two components were - analyzed and the one component was found to be a mixture of powdered magnesium and powdered aluminum, with potassium chlorate as the second component.

Flash powders, when mixed, are extremely flammable and shock sensitive and, if covered or placed in a closed container, are explosive. Mix only in plastic containers with plastic utensils and with great caution. Mix only as much as you plan to use and **never store mixed flash powder**. Once mixed the material is unpredictable and should be used immediately.

DRAGON'S BREATH

Dragon's Breath is available from magicians' supply stores. When sprayed into a fire, it burns producing a large billow of flame like a dragon's breath. This is the material a magician uses to produce a puff of flame from his/her hand.

Dragon's breath is composed of lycopodium, a fine yellowish powder which is composed of club-moss spores (available from many laboratory supply houses). The process of spraying it into a fire results in a dust explosion as the fine particles burn when heated in an abundance of fresh air. It can be demonstrated that lycopodium does not burn in bulk by attempting to burn a small pile of it on a ceramic or other flame proof board. Lycopodium can be sprayed from a plastic wash bottle, a small rubber bulb, or simply thrown into a flame.

Care should be exercised in using lycopodium powder as some individuals are allergic to the spores.

SNAKES

Magic Snakes, sometimes called Pharaoh's Serpents, come as small pellets which, when ignited, "grow" into long curving columns of ash resembling a "snake". Originally, snakes were composed of mercury(II) thiocyanate, $Hg(CNS)_2$, which was bound into a pellet by using dextrin or a gum. Due to the toxic nature of the mercury(II) thiocyanate and of the combustion products, sulfur dioxide and mercury vapors, the mercury compound has been replaced. The black, non-mercury snakes now available are composed of a naphthol pitch that has been mixed with linseed oil, treated with nitric acid, washed and air dried, then broken up and further treated with picric acid. The product is then mixed with gum arabic, pelleted, dried, and aged for several months.

CAPS AND BLASTER BALLS

Caps used in cap guns usually contain 0.20 grains or less of a pyrotechnical material composed of potassium chlorate, $KClO_3$; red phosphorus, P_4; manganese dioxide, MnO_2; magnesium oxide, MgO or calcium carbonate, $CaCO_3$; sand, SiO_2; and glue to bind it together. The manganese dioxide catalyzes the decomposition of potassium chlorate to form oxygen and potassium chloride. The magnesium oxide or calcium carbonate acts as an anti-acid to prevent deterioration due to moisture in storage. The sand helps to produce friction. The mixture of potassium chlorate and phosphorus is explosive and extremely unpredictable in any quantity.

A variation of the caps used in cap guns are called Blaster Balls marketed by Placo Products Co., Cosmos®, and others. These consist of a set of two ceramic balls of different colors (usually yellow and black, or red and blue), which are both coated with a thin layer of the same chemical mixture of potassium chlorate, sulfur, glue, and - powdered glass (silica). To use Blaster Balls, holding one ball in the hand, toss the other ball into the air and catch it by bringing the hand with the ball upward cracking the balls together. When the coated surfaces of the two balls hit together, there is a cap-like blast produced. The same cap-like blast can be produced if a single ball hits a high silica-containing substance, such as concrete, indicating that the silica produces sufficient friction, and heat, to detonate the chemical mixture. A pair of Blaster Balls can produce over 200 blasts. (NOTE: Although Blaster Balls are non-flammable, a mixture of potassium chlorate and sulfur is explosive and is unpredictable in any quantity.)

SNAP'N POPS

Snap'n Pops, also called Devil Bangs, Rio Snappers, or Bang Snaps are noisemakers made in Brazil or Korea. A Snap'n Pop is a cigarette paper rolled and twisted into the shape of a roughly spherical teardrop with a tail. The teardrop is loaded with about 0.18 gram of small gravel or coarse sand coated with 0.0008 gram of silver fulminate, $Ag_2(CNO)_2$. When the device is thrown against a hard surface, friction between the granules sets off the silver fulminate with a quick bang.

The explosion generates little flame and almost no gas, as compared with toy caps, so that the granules are not widely scattered. Except for the paper wrap, they are nonflammable. They are safe in storage and shipment. They are not set off by heating to 75°C (167°F) but will detonate if exposed to a flame. Even when detonated in the hand, it causes no burn, tingle, or damage.

BIG-BANG® CANNONS

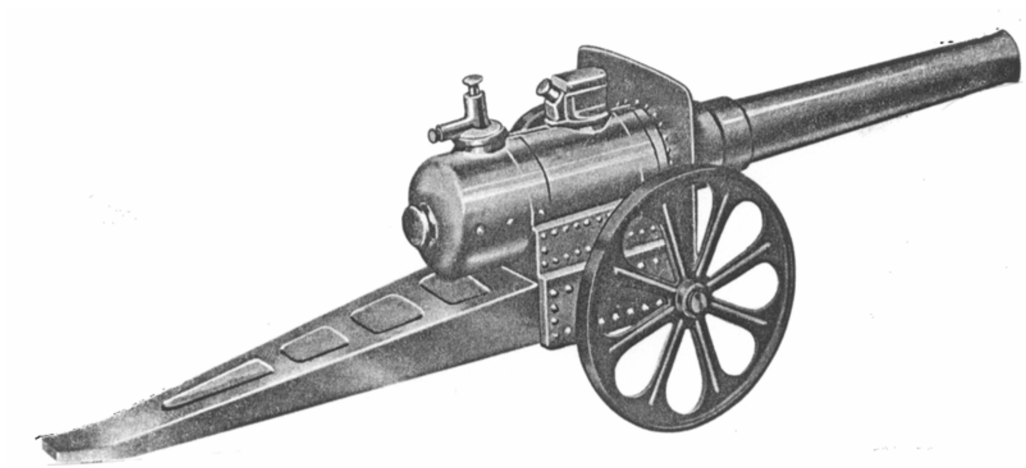


Figure 25. A Big-Bang® Cannon

A Big-Bang® Cannon (see Figure 25), made by The Conestoga Company, Bethlehem, Pa., is fueled by a substance called Bangsite®. Bangsite® is powdered calcium carbide. The Bangsite® is placed in a breech block on the cannon and a small amount is emptied into the firing chamber which contains a small amount of water. On reaction with water, acetylene is produced:

$$\underset{\text{calcium carbide}}{CaC_2} + H_2O \rightarrow \underset{\text{calcium oxide}}{CaO} + \underset{\text{acetylene}}{C_2H_2}$$

The acetylene produced mixes with the oxygen in the air within the firing chamber. When a spark is produced by the firing mechanism, the acetylene gas burns rapidly to produce carbon dioxide and water vapor according to the reaction:

$$2\,C_2H_2 + 5\,O_2 \rightarrow 4\,CO_2 + 2\,H_2O$$

This rapid burning produces heat resulting in the almost instantaneous expansion of the gases forcing them out of the muzzle of the cannon. The combustion of the remaining gases is completed outside of the cannon leaving a -

partial vacuum outside the muzzle and within the cannon. The resulting “inrush” of the atmosphere to fill the void is perceived as an explosion producing a loud bang or noise. (see Figure 26)

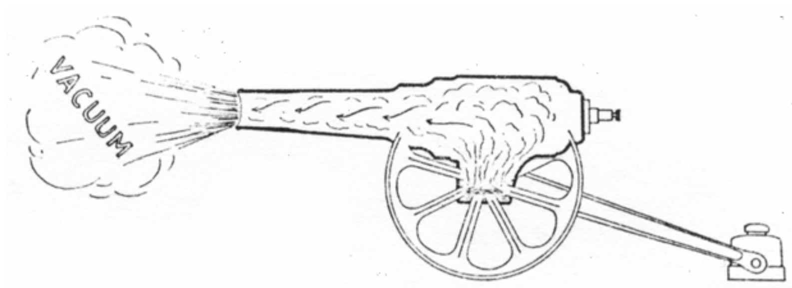


Figure 26. Firing the cannon