Smokes: The How And The Why



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Who Was That Masked Man?

- Crackerjacks, Inc.
 - Vice President for Publications
 - Webmaster : <u>www.crackerjacks.org</u>
- Department of the Army

 Chief, Pyrotechnics Team (26 years)
 LTC Maryland Army National Guard

Typical Black Powder Analysis

Potassium Nitrate	(KNO3)	74.43
Charcoal	(C)	14.29
Sulfur	(S)	10.09
Water	(H2O)	1.06
Potassium Sulfate	(K2SO4)	0.13





K2/3024 S 0L.119%4 0.1% 14.3% KNO3 74.4%

Typical Black Powder Analysis

It's hard to believe that less than 50% of the combustion products are gases.

Combustion Products Weight%

Solids Gases Water 55.91 42.98 1.11





Typical Black Powder Analysis

ny doubts of the composition of the white residue?

Solids		Weight%
Potassium Carbonate	K2CO3	61.03
Potassium Sulfate	K2SO4	15.10
Potassium Sulfide	K2S	14.45
Sulfur	S	8.74
Potassium Nitrate	KNO3	0.27
Potassium Sulfur Cyanide	KSCN	0.22
Ammonium Carbonate	(NH4)2C	O3 0.08
Carbon	С	0.08



Smokes were developed for **what** reason???



Arthasastra

Published 300 BC by Kautilya

Provides formulas for poisonous smokes

Made from Green Vitriol (arsenic sulfides) Poison

- plants
- insects
- animals
- reptiles



Wu Pei Chih 80 volumes of 240 chapters (Records of War Preparations)

To make a powder producing much smoke:

- 1 pound saltpeter
- 1 pound shih huang
- 4 ounces of sulfur
 - boiled in human urine
- 4 ounces p'ishuang
- 1 ounce ch'ang nao
 - (deer brains)
- 1/10 ounce ch'ing fan



Pyrotechnic Smoke Mixture for Defending Thick Walls Against Attack.

An apple sized ball is dropped into the excavation tunnel built by the enemy.

Formula given as :

30 lb resin 30 lb saltpetre 10 lb sulfur 6 lb charcoal 10 lb arsenic



Dialogus oder Gesprach zweier Personen... Published 1573 by Samuel Zimmerman

Describes "amusement" smokes consisting of:

SaltpeterSulfurMercury



British Old Smoke Ammo Design

Candle, Smoke, M1, Type S o 3 5/8" diameter • 5" high 3 min burn time 2 1/2 lbs payload Potassium Nitrate Sulfur Pitch Yellowish brown smoke Borax - Glue

Torch, Smoke, M1

White smoke with a "tinge" of yellow

4 min burn time

Composition	PBW
Potassium nitrate	47.4
Pitch	29.2
Borax	10.6
Calcium carbonate	4.9
Sand	4.0
Sulfur	3.9



188,102 of the 500,000 ordered were ever made.

Edgewood Arsenal 1920

Hexachloroethane now cheap to make
Needed solid ingredients only
BM candles @ 60 deg C die in 5 weeks

	M-III mix	BM mix
Zinc powder	32.8	35.4
Carbon tetrachloride		41.6
Hexachloroethane	39.8	
Sodium chlorate	17.0	9.3
Ammonium chloride	7.4	5.4
Magnesium carbonate	3.0	8.3

Blend 7:1 with carbon tetrachloride and let evaporate

Edgewood Arsenal 1920 Candle, Smoke, HC, M1

600,000 obsolete canisters

- Let's use 'em for smoke!
- now pressed hydraulically
- Could not seal the can properly
- continued development using.....
 - the old gas mask canister!!!

Hexachloroethane	50
Zinc powder	28
Zinc oxide	22

1 lb 13 oz



Edgewood Arsenal 1926 Grenade, Hand, Smoke, HC, M8

Chief of Infantry speaks out
Standardize the cans
3/4 to 1 3/4 lb
2 1/8" to 2 3/8" diameter
4" to 5" long



	Fast 50 gm	Slow 535 gm
Zinc dust	36	36
Hexachloroethane	43	44
Ammonium perchlorate	15	10
Ammonium chloride	6	10

1933, Chief or Ordnance renames Candle Smoke, HC MII to Grenade, Hand, HC, M8



HC Smoke Mixes

	M3	M1	Slow	Fast	Type C	Type D
Zinc	32.8	28	36	36		
Zinc Oxide		22			46.5	43.4
Ammonium Chloride	7.4		10	6		
Sodium Chlorate	17.0					
Magnesium Carbonate	3.0					
Hexachloroethane	39.8	50	44	43	46.5	50.6
Ammonium Perchlorate			10	15		
Aluminum					7.0	6.0

HC Smoke Mixes

	Type D
Zinc Oxide	43.4
Hexachloroethane	50.6
Aluminum	6.0



Classes of Particulate Clouds

Dusts - formed by mechanical disintegration
 0.1 - 100 microns

Mists - formed by condensation of liquids 5-10 microns

Fogs - high concentration of mist droplets
 (must be visible to naked eye)

Smokes - any particle suspension
not classified as a dust or mist
(0.01 to 5.0 microns)



Optical Properties









Smoke Cloud Destruction

Evaporation/Condensation

Droplet size is critical

 Droplets smaller than critical diameter will evaporate because their vapor pressure is higher than the partial pressure in the vapor phase.

 Droplets larger than the critical diameter will grow as a result of condensation.

Also applies to small solid particles.

Zinc / Sulfur Smoke



Zinc / Sulfur / Potassium Chlorate



Zinc / Ammonium Perchlorate



Color

Visibility



Duration



Persistence

Volume

Signalling

Target Acquisition

Identify specific targets on the battlefield







Chemical Dissemination

Specific chemicals for types of smoke Insecticides Reforestation Plant coatings (smudge pots)

Riot control agents

Toxic agents



Fire Reproduction

In combat for deception

In movies for special effects





Nuisances

 Undesirable for cannons/guns due to lack of gas production and as heat sink

Gives away firing position

Unable to see civilian fireworks during displays

Magnesium / Hexachloroethane



Magnesium / HC / NP



Loading Force vs Burn Time

Compacted devices fall into two basic categories,

Pressed devices
 Cast devices.

Compacted pyrotechnic compositions are universally loaded with the use of a hydraulic ram instead of the older "hammer wack" technique. By keeping increments small in relation to the container height, the cross sectional density of the material will be more uniform and the resulting device more reliable.



Loading Force vs Burn Time

Loading	Burn Time	Efficiency
Pressure	(seconds)	(percent)
(pounds)		
0	2.0	100
5,000	5.0	183
10,000	9.0	226
15,000	9.5	219
20,000	10.0	256

BT Versus Fuel:Oxidizer Ratio

Fuel	Oxidizer	Burn Time
	1.0	
1.0	1.0	I'/ sec
1 0	1 75	1/
1.0	1./3	14 Sec
1.0	2.5	10 sec

Sucrose: Potassium Chlorate System

Burn Time vs Exit Orifice Diameter

Orifice Diameter	Burn Time	Smoke Efficiency
(inches)	(Seconds)	(percent)
.172	7.6	104
.190	8.5	104
.205	9.3	106
.250	12.2	115

Burn Times vs Granule Size

Mesh Size	Granule Diameter (microns)	Burn Time (seconds)	Smoke Efficiency (percent)
325	45	10	93
60	250	7	100
10	2000	5	93

Catalyst Effects vs Burn Time

Catalyst	Burn Time	Efficiency
	(seconds)	(percent)
None	10	100
Copper Chloride	9	101
Iron Sulfide	8	96
Iron Acetate	7	102
Red Iron Oxide	7	105

Sucrose: Potassium Chlorate System
Colored HC Smoke

Magnesium	16
Hexachloroethane	14
Red Iron Oxide	36



HEXACHLOROETHANE BASED ORANGE SMOKE

Colored HC Smoke

Magnesium	16
Hexachloroethane	14
Red Iron Oxide	36
Magnesium Carbonate	+10



HEXACHLOROETHANE BASED ORANGE SMOKE

2 Component Black Smoke

Polystyrene

Potassium Chlorate



	Yellow	Orange	Brown
Magnesium	14	15	15
Potassium Dichromate	66	35	
Bismuth Tetroxide	20		
Lead Dioxide		50	35
Cupric Oxide			50

	Yellow
Magnesium	14
Potassium Dichromate	66
Bismuth Tetroxide	20



	Yellow
Magnesium	14
Potassium Dichromate	66
Bismuth Tetroxide	20
Magnesium Carbonate	+10



	Orange
Magnesium	15
Potassium Dichromate	35
Lead Dioxide	50



	Orange
Magnesium	15
Potassium Dichromate	35
Lead Dioxide	50
Magnesium Carbonate	+10



	Brown
Magnesium	15
Lead Dioxide	35
Cupric Oxide	50



	Brown
Magnesium	15
Lead Dioxide	35
Cupric Oxide	50
Magnesium Carbonate	+10



Red Dye Based Colored Smoke

	CARCINOGENIC RED SMOKE	STANDARD RED SMOKE	RED SMOKE III	NEW SAFER RED SMOKE
Wheat Flour	15.0 pbw			
Sulfur			9.0 pbw	
Lactose		18.0 pbw		
Sucrose				17.5 pbw
Potassium Chlorate	25.0 pbw	29.5 pbw	26.0 pbw	17.5 pbw
Rhodamine B	24.0 pbw			
Para Red	36.0 pbw			
Red Dye		47.5 pbw	40.0 pbw	
Dye, Disperse Red 11				6.8 pbw
Dye, Solvent Red 1				34.2 pbw
Sodium Bicarbonate			25.0 pbw	
Magnesium Carbonate		5.0 pbw		10.0 pbw
Terephthalic Acid				14.0 pbw

Safer Red Dye Based Colored Smoke



Yellow Dye Based Colored Smoke

	STANDARD YELLOW SMOKE	YELLOW SMOKE IV	NEW SAFER YELLOW SMOKE
Wheat Flour			
Sulfur		8.5 pbw	
Lactose	16.0 pbw		
Sucrose			15.0 pbw
Potassium Chlorate	26.5 pbw	20.0 pbw	22.0 pbw
Benzanthrone	32.0 pbw	24.5 pbw	
Yellow Dye	14.0 pbw	14.0 pbw	
Dye, Solvent Yellow 33			33.0 pbw
Sodium Bicarbonate	33.0 pbw	33.0 pbw	
Magnesium Carbonate			21.0 pbw

Safer Yellow Dye Based Colored Smoke



Green Dye Based Colored Smoke

	CARCINOGENIC GREEN SMOKE	OLD STANDARD GREEN SMOKE	GREEN SMOKE IV	NEW SAFEF GREEN SMOI
heat Flour	15.0 pbw			
ılfur			10.4 pbw	
ctose		18.0 pbw		
icrose				16.5 pbw
otassium Chlorate	28.0 pbw	31.5 pbw	27.0 pbw	24.5 pbw
Iramine	10.0 pbw			
ethylene Blue	17.0 pbw			
digo Pure	30.0 pbw			
enzanthrone		9.4 pbw	8.0 pbw	
een Dye		32.9 pbw	28.0 pbw	
ellow Dye		4.7 pbw	4.0 pbw	
e, Solvent Yellow 33				12.5 pbw
e, Solvent Green 3				29.5 pbw
dium Bicarbonate			22.6 pbw	

Safer Green Dye Based Colored Smoke



Violet Dye Based Colored Smoke

	CARCINOGENIC	STANDARD	NEW SAFER
	VIOLET SMOKE	VIOLET SMOKE	VIOLET
			SIVIORE
Wheat Flour	15.0 pbw		
Sulfur			
Lactose		24.0 pbw	
Sucrose			19.1 pbw
Potassium Chlorate	26.0 pbw	22.0 pbw	18.4 pbw
Indigo Pure	22.0 pbw		
Para Red	21.0 pbw		
Rhodamine B	16.0 pbw		
Violet Dye		46.0 pbw	
Dye, Disperse Red 11			38.0 pbw
Dye, Disperse Blue 3			4.4 pbw
Sodium Bicarbonate			
Magnesium Carbonate		7.0 pbw	20.1 pbw

Safer Violet Dye Based Colored Smoke



Unusual Dye Smokes

Guanidine Nitrate Based

Guanidine Nitrate	40
Celluloid Powder	35
Dye	25

2 Component Smoke

Polybamo	50
Dye	50

Plastic Bonded Colored Smoke

Sucrose	18.0
Potassium Chlorate	23.0
Dye	51.0
Potassium Dichromate	8.0
Polyvinyl Acetate	2.2
Dichloromethane	5.8

Smoke Fuel Mix

UNIVERSAL SMOKE FUEL MIX

Sucrose	28
Potassium Chlorate	40
Magnesium Carbonate	32



Fast Smoke Fuel Mix

UNIVERSAL SMOKE FUEL MIX

Sucrose	28
Potassium Chlorate	40
Magnesium Carbonate	5



Slow Smoke Fuel Mix

Sucrose28Potassium Chlorate40Magnesium Carbonate15



Sucrose / Potassium Chlorate

Straight Binary Mix

Sucrose28Potassium Chlorate40



Vaporized Wax Smokes



Vaporized Wax Smokes

Sucrose	19
Potassium Chlorate	29
Magnesium	6
Carbonate	
Synthetic Wax	46



Future Low Toxicity Smokes



Future Low Toxicity Smokes

Sucrose	14
Potassium Chlorate	23
Magnesium	6
Carbonate	
Terephthalic Acid	54



Where is the Peanut Butter Smoke ???





Sucrose	28
Potassium Chlorate	40
Magnesium Carbonate	32











The stoiometric blended composition begins at a burn time of 24 seconds for a hand sized device.



Burn Tim

By decreasing the fuel/oxidizer ratio the burn time is reduced to 18 seconds. This increases the available oxygen to the fuel due to brute force.



A burn time of 9 seconds is then achieved by reducing the smoke material in the composition. This works well as there is now less of a "heat sink" material in the device.



A one second drop in burn time to 8 seconds is possible with the addition of ten percent by weight of fine powdered aluminum. This improves the thermal conduction of the composition while providing a highly energetic fuel.



• A burn time of 7 seconds is possible when the exit orifice diameter is reduced from 0.3125" to 0.1875" in diameter. The increased back pressure increases the rate of reaction.



A 6 second burn time is achieved by increasing the amount of material ignited at the beginning of the burn. The center core diameter is enlarged from 0.312" to 0.500 inches in diameter.


Fast Burning Smoke Item Design

By adding 2 percent of iron oxide the burn time drops to 3 seconds. The catalytic effect causes a 50% reduction in the burn time.



← Burn Tim

Fast Burning Smoke Item Design

Finally, by pressing the composition into 1/8" by 1/8" pellets and placing them in the same container, the burn time drops to a low of 1.8 seconds. Any additional drop in the burn time will destroy the integrity of the canister.



━━ Burn Tim ━━ Efficienc

Fast Burning Smoke Item Design

Modification	Burn Time	Efficiency
	(seconds)	(percent)
Basic Mix	24.0	100
Decrease Fuel	18.0	87
Decrease Smoke	9.0	65
Thermal Conductor	8.0	63
Pressure	7.0	71
Surface Area	6.0	61
Catalyst	3.0	67
Particle Size	1.8	53



Cast HTPB Propellants



Cast HTPB Colored Flames



Red

Purple



Cast HTPB Based Smokes



White Smoke

Black Smoke



Accident Summary

for Pyrotechnic Mixtures*

Type	Number	Percentage
Primers	12	2.0
Flares	21	3.6
Smokes	385	66.8
Gas	35	6.0
Noise	7	1.3
Heat	59	10.3
Delays	2	0.3
End Items	56	9.7

40% of all accidents were during pressing



Go, Make Smoke, and Stay Green!

