

**ALTERNATIVE OXIDANTS
AND PROCESSING
PROCEDURES FOR
PYROTECHNIC TIME
DELAYS**

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SYNOPSIS

This study was directed at the pyrotechnic time delay compositions that are used in detonator assemblies. The objectives were to:

- Investigate effective alternatives for the barium and lead-based oxidants currently used, maintaining the use of silicon as fuel
- Develop easy to use, realistic measurement techniques for burn rates and shock tube ignitability
- Determine the variables that affect burn rate, and
- Evaluate alternative processing routes to facilitate intimate mixing of the component powders.

Lead chromate and copper antimonite were found to be suitable oxidants for silicon in time delay compositions. They were ignitable by shock tubing, a relatively weak ignition source. The measured burn speeds for these systems showed a bimodal dependence on stoichiometry. Measured burn rates varied between 6-28 mm/s. Lead chromate is potentially a suitable alternative to the oxidant currently used in the

medium burn rate commercial composition. It burns faster than copper antimonite. The latter is potentially a suitable replacement oxidant for the *slow* and *medium* compositions.

Antimony trioxide-based compositions exhibited unreliable performance with respect to ignition with shock tubing.

The addition of aluminium powder or fumed silica was found to reduce the burn rate. Increasing the silicon particle size ($<3,5\mu\text{m}$) also decreased the burn speed for copper antimonite and lead chromate compositions. Addition of fumed silica improved the flow properties of the lead chromate, copper antimonite and antimony trioxide powders allowing for easier mixing.

The silicon powder was found to react violently with water in alkaline solutions. This makes particle dispersion in a wet-mixing process problematic.

Keywords: pyrotechnic, time delay, copper antimonite, burn speed, silicon, lead chromate, antimony trioxide, detonator.

ALTERNATIEWE OKSIDEERMIDDELS EN PROSESSERING VAN PIROTEGNIESE TYD VERTRAGERS

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SINOPSIS

Hierdie studie was gerig op pirotegniese tydvertragersamestellings wat in slagdoppies gebruik word. Die doelwit was om:

- Effektiewe alternatiewe vir die barium- en loodgebaseerde oksideermiddels te vind wat tans saam met silikon as brandstof gebruik word
- Eenvoudige en realistiese meettegnieke vir ontsteekbaarheid en die brandtempo van tydvertrager formulasies te ontwikkel
- Te bepaal watter veranderlikes brandtempos beïnvloed, en
- Alternatiewe prosesserings roetes te ondersoek om goeie vermenging van die komponentpoeiers te verseker.

Dit is gevind dat loodchromaat en koperantimoniet geskikte oksideermiddels is vir silikon in tydvertragensamestellings. Hulle kon ontsteek word met behulp van 'n skokbuis, 'n relatief lae intensiteit ontstekingsbron. Die brandtempos toon 'n bimodale afhanklikheid van stoichiometrie. Die gemete waardes het variëer oor die gebied 6-28 mm/s. Loodchromaat is 'n potensiële alternatiewe vir die oksideermiddels wat tans in die "medium" kommersiële samestelling gebruik word. Dit brand

vinniger as koperantimoniet. Laasgenoemde is 'n potensiële alternatief vir die oksideermiddels in die “stadige” en “medium” samestellings.

Antimoon trioksied gebaseerde samestellings het wisselende resultate in terme van aansteekbaarheid met skokbuise getoon.

Toevoegings van aluminium of gerookte silika poeiers het brandtempos verlaag. Die brandtempos van die koperantimoniet en loodchromaat samestellings het ook afgeneem met toename in die silikon partikelgrootte. Gerookte silika het ook die vloei eienskappe van loodchromaat, koperantimoniet en antimoontrioksied poeiers verbeter en sodoende beter vermenging bewerkstellig.

Silikon reageer heftig met water in die teenwoordigheid van alkalies. Dus is die dispersie van die partikels in 'n nat vermengingsproses problematies.

Sleutelwoorde: pirotegnies, koperantimoniet, brandtempo, silikon, loodchromaat, antimoontrioksied, slagdoppie

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NOMENCLATURE

a	Filtration parameter for first order data filter
a_0	Initial thickness of metal A (half effective particle size of the discontinuous phase (cm)
b	Reaction zone width
b_1	Fraction of inert or product diluent
c	Specific heat capacity
c_1	Heat capacity of the gaseous products
c_p, c_s, c_f	Specific heat capacity of solid
d	Particle size
d_1	Particle size of fine particles
d_2	Particle size of coarse particles
d_B^{st}	Diameter of reactant B in a corresponding stoichiometric mixture
d_{eff}	Effective particle size
d_{max}	Maximum particle size
d_{min}	Minimum particle size
D	Mass diffusivity
D_{rc}	Diameter of the reaction cell.
E	Activation energy
f	Fraction of the surface covered by the adsorbate
f(d)	Dependence of v on particle size
f(n)	Reaction order function
F	Van der Waal's force between particles
F(T)	Dependence of v on temperature
G	Thermal power arising from heat effects of all changes
h	Lateral heat transfer coefficient
H_R	Heat of reaction at 298K
H_f	Heat of formation at 298K
k	Boltzmann constant
K_{ads}	Adsorption constant
K_0	Preexponential constant for kinetics
l	Order of reaction

L	Distance between centres of two particles
Le	Lewis number
m	Combustion mass velocity
m_1	Mass fraction of fine particles
MW_i	Molecular mass of component i
n	Reaction order
P	Vapour pressure of most volatile component or product dissociation pressure at the combustion temperature
P_o	External gas pressure
Q	Heat of reaction
r	Radius of spherical particle
R	Ideal gas constant
s	Distance between two particles
S	Surface area
t^*	Rise time of inert forewave
t_{th}	Thermal relaxation time
T	Absolute temperature
T^*	Conversion controlling the combustion front
T_a	Ambient temperature
T_c	Combustion temperature
T_f	Flame temperature
T_g	Gas temperature
T_m	Melting point
T_s	Condensed phase temperature
T_0	Initial temperature of porous solid
u	Attraction energy
U	Temperature excess
v	Velocity of the combustion front
v_1	Mass fraction of gas in the reaction products
v_i	Volume of component i
w	Rate of heat evolution per unit mass of reaction mixture
w_1	Thickness ratio of metals A and B
W	Constant for calculation of van der Waal's forces
W_1	Energy required to produce a dispersion

x	Spatial coordinate in travelling wave frame
x_T	Characteristic length of thermal relaxation in combustion wave
x_n	Measured value at time n .
y	Reaction velocity
y_n	Filtered value corresponding to x at time n
y_{n-1}	Filtered value corresponding to x at time $n-1$
α	Tamman temperature ratio
α_1	Thermal diffusivity
α_2	Coefficient of interphase heat transfer
β_1	Heating rate
β_2	Pore shape parameter
β, γ	Wave stability parameters
$\chi(d)$	Particle size distribution
δ	Product layer thickness
δ_1	Length which surfactant extends into liquid
ϕ	Volume fraction of component
γ_1	Surface tension
η	Reactant conversion
η^*	Conversion controlling the combustion front
η_1	Degree of reaction
ι	Confinement parameter (fraction of the gas that passes through the flame)
λ	Thermal conductivity
ρ	Density
ρ_0	Initial effective solid density (mass per unit volume of porous solid)
ρ_∞	Final effective solid density (fully reacted)
ξ	Gas direction flow parameter