

FINAL REPORT

EVALUATION OF US AND UN TEST PROCEDURES FOR DETERMINING SHIPPING HAZARDS OF SOLID OXIDIZERS

By N. B. Greninger, G. F. Friel, and T. C. Ruhe

NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH

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For

U.S. DEPARTMENT OF TRANSPORTATION

Research and Special Programs Administration
Office of Hazardous Materials Safety
400 Seventh Street, SW
Washington, DC 20590 - 0001

Under

DOT / NIOSH Interagency Agreement: DTRS56-95-X-0029

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*****ABSTRACT**

An evaluation study of UN and US test procedures for solid chemical oxidizers (SCOs) was performed by the National Institute for Occupational Safety and Health (NIOSH) for the US Department of Transportation (DOT). Eighteen solid oxidizers were mixed with cellulose (UN test) and fourteen with sawdust (US test). Burning times were compared with those from reference mixtures.

Twenty-nine percent of the UN published hazard classifications were confirmed using potassium bromate (KBrO_3) with a particle size from 150 to 300 μm . For sizes of this carcinogen less than 150 μm , 71% were confirmed. In tests with the proposed noncarcinogenic potassium chlorate (KClO_3) reference less than 300 μm in size, 76 % of the classifications were confirmed. Classifications that were based on the US protocol, using three different reference chemicals specified were confirmed for 21 % of the cases.

The data provides a basis for adopting a modified version of the UN protocol featuring the replacement of the bromate standard with potassium chlorate. If it is decided to retain the US protocol, then similar changes are recommended. There would be then only minor differences between the US and UN protocols. Proposed future work is discussed, including modeling, information retrieval, particle size effect on burn time, and the reactivity of liquid oxidizers in open and semi-confined environments. Approximately 800 combustion tests were conducted.

***EXECUTIVE SUMMARY

A study of US and United Nations test procedures for the classification of solid chemical oxidizers (SCOs) for shipment was performed by the Pittsburgh Research Laboratory (PRL) of the National Institute of Occupational Safety and Health (NIOSH) for the US Department for Transportation (DOT). The objectives were to evaluate and compare the two procedures and to classify appropriate oxidizers according to the UN and US procedures. The UN test procedure for the classification of oxidizing solids requires the measurement of the combustion time of a solid oxidizer mixed with dry fibrous cellulose. The US test method for solid oxidizers uses softwood sawdust in place of cellulose.

The UN test procedure makes use of potassium bromate as the sole reference SCO and precisely specifies the size cut (150 to 300 μm) to be used in preparing mixtures of the three different mass ratios of SCO-to-cellulose. It further calls for the use of cellulose with a fiber length between 50 and 250 μm and a mean diameter of 25 μm . Conical shaped piles with mass ratios of SCO to cellulose of 1:1 and 4:1 are each ignited by an ignition wire shaped in the form of an indented but open circle. The wire is heated at 150 watts throughout the test, and the burn time is measured from the application of power to the wire to the cessation of combustion for the main body of the mixture.

Presently, the US test procedure involves mixing samples of each SCO that will pass through a sieve mesh size smaller than 300 μm with softwood sawdust that will pass through a sieve mesh size smaller than 1,600 μm (1.6 mm). Conical shaped piles with mass ratios of SCO to sawdust of 1:1 and 4:1 are each ignited by a circular ignition wire (whose bare wire temperature is 1,000 °C) which is positioned close to a low-heat-conducting refractory surface near the bottom of the pile. The power is terminated once combustion gets underway. The US burn time is measured from the onset of combustion (open flaming or smoking) to the cessation of combustion for the main body of the mixture.

Because most of the SCOs are health hazards, the samples are prepared in an exhaust hood and the combustion process is carried out in the ventilation hood with the laboratory personnel using respirators, safety goggles, and other appropriate safety equipment. In addition the mixtures of SCOs and fuels are highly reactive and can pose serious risks to personnel if ignition of these mixtures occurs

unexpectedly. The explosion risk and violence of the reactions, should they occur, become compounded as the degree of confinement of the mixture is increased. Careful preparation and caution in conducting these tests are, therefore, mandatory.

Eighteen solid oxidizers were mixed with cellulose and fourteen solid oxidizers were mixed with basswood sawdust in different mass proportions to classify the hazards of these oxidizers. The burning times of the mixtures were compared with those of reference mixtures to determine the Packing Group classification assignment of the oxidizers. Some mixtures were also prepared with the SCO having various degrees of fineness to evaluate the variability in the mean burn time and the classification rating dependence on the fineness of the SCO. Some mixtures were prepared from (1) coarse, as shipped, SCOs; (2) SCOs ground by mortar and pestle (M & P); (3) SCOs ground in a "food processing" mill; and (4) very fine, as shipped SCOs (less than 104 μm). Although most of the fuels that were mixed with the SCOs were either cellulose or basswood sawdust, a few other fuels were considered - yellow pine sawdust and wood flour (a very fine sawdust) in exploratory studies to perfect laboratory procedures, and to study the relationship of the mean burn time with the power applied to the heater wire. Approximately 800 combustion tests with SCO/fuel mixtures were conducted.

Eleven out of 38 UN classifications (29 %) were confirmed using the UN procedure involving KBrO_3 of a particle size range from 150 to 300 μm for the 3:7, 2:3, and 3:2 reference mixtures. When UN reference mixtures were made using KBrO_3 powder less than 150 μm , 27 out of 38 classifications (71 %) were confirmed. When the UN classifications were based on published example times of 100 seconds, 54 seconds, and 4 seconds for bromate / cellulose standards, and NIOSH experimental data were used, 30 out of 38 classifications (79 %) were confirmed. When classifications were made based upon the 3:7 and 2:3 standards made from KBrO_3 of the 150 to 300 μm particle size cut and 3:2 standard made from KBrO_3 less than 150 μm particle size, the Packing Group demarcation burning times agreed well with the UN published example times.

In classifying a SCO it is important to standardize the procedure and to ensure that the test outcome is not operator dependent. The reliability of the Packing Group assignment is often best

assessed by running appropriate tests with the reference mixtures and comparing the mean burn time of the material being classified with those from the reference standards. To avoid or reduce the contamination of the laboratory work area with the carcinogen, KBrO_3 , its use as a reference standard should be minimized. Therefore, an alternative noncarcinogenic UN reference oxidizer, KClO_3 , was evaluated as a replacement for KBrO_3 . With the proposed KClO_3 reference standard set [made using a SCO with particle size cut less than **300** μm and mass ratios of **1:7**, **1:5**, and **2:1**], **29** out of **38** classifications (**76 %**) agreed with the published UN ones.

Packing Group classifications, based on the US test procedure and PRL experimental data using the set of potassium bromate, potassium perchlorate, and ammonium persulfate standards, gave agreement with US published values in only **three** out of **14** classifications (**21 %**). Packing Group classifications, based on US test procedures and a proposed set of potassium chlorate / basswood standards (**80** seconds for **2.2:10**, **50** seconds for **3:10**, and **11** seconds for **2.53:1** for the SCO less than **300** μm) gave agreement with published US values in **seven** out of **14** classifications (**50 %**). [Had the KClO_3 been finer, say less than **150** μm , then the time associated with the **2.53:1** ratio would have been closer to **5** seconds, resulting in better classification agreement.]

Although the US procedure, requiring **three** tests, was less time consuming than the UN procedure, which required **five** tests, it generally yielded higher standard deviations for the mean burning times than the UN procedure. The replications in the US procedure should be increased so that at least **five** tests each are conducted for **1:1** and **4:1** mixtures and the standards. The placement of the ignition wire under the pile for both procedures produced considerable redistribution of several of the mixtures during burning, resulting in either high standard deviations or "artificially" low values for the mean burning time. To better control scatter of the mixture during the initial stages of burning and better control the fraction of the **30**-gram oxidizer/ fuel mixture participating in the burn, either a restraining ring of about **2.5** cm in height should be placed around the pile and/or another location for the igniter wire should be considered.

More uncertainty existed in the UN definition of burning time than existed in the US definition of

burning time for the less reactive oxidizers. The use of cellulose in the UN procedure significantly improved its reliability and reproducibility. It is recommended that both procedures be refined and different sets of reference oxidizers be considered. The US procedure could be significantly improved by replacing the < 1,600 μm sawdust with cellulose of particle size (average being 125 μm) similar to that used in the UN test procedure. Doing this would significantly reduce the standard deviation for the mean burn time. The oxidizer, KClO_3 of adequate fineness, with the choice of an appropriate set of oxidizer to fuel ratios could serve as a suitable replacement for KBrO_3 in the UN procedure and as a suitable replacement for KBrO_3 , KClO_4 , and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in the US procedure. The use of a video camera to record the combustion process was of significant help in analyzing the test results.

There is a need to identify a statistical criterion for rejection of an outlier and establish criteria to determine whether additional tests are needed. There is also a need to identify the number of replications needed, taking into account the standard deviation, that will enable a comparison of means to be made in a manner that is in accord with standard statistical procedures. This entails primarily the application of the F-test and t-test. Special consideration ought to be given to what levels of significance (α) are appropriate in dealing with SCOs.

The analysis of the experimental data and consideration of health properties of SCOs provides an adequate basis to advocate that the US adopt a "refined" version of the UN test protocol for SCOs which entails among other things replacing the three potassium bromate / cellulose mass ratios used as standards with three potassium chlorate ones. If it were decided that in the "interim" or "transitional" time period for adopting the UN test protocol that the US test protocol be also utilized, then some key changes should be made. These include replacing the current set of **three** reference standards (potassium bromate, potassium perchlorate, and ammonium persulfate) with potassium chlorate at **three** different oxidizer-fuel mass ratios, and increasing the sample size number to at least **five**. If DOT were to advocate replacing the sawdust with cellulose of the fineness used in the UN test protocol, then there would be only minor differences between the refined US and UN test protocols.

To avoid laboratory contamination when conducting tests, care should be taken to select a

ventilation hood of adequate design and size. It should have an all stainless steel interior with integral trough and cup sink drains and water faucets; and it should also have a bottom airfoil. A perchloric acid wash down type hood is preferred. For the more energetic oxidizers, exploratory classification tests should be conducted with less than **30**-gram mixtures to avoid having the combustion products and unreacted components jet out of the hood into the laboratory. Because of the potential violence in conducting SCO-fuel reactions, a plastic safety shield should be employed when mixing reactants and conducting burn tests; such would protect the body and head from flying glass from the hood should the material react unexpectedly or with great violence. A hazard assessment model for use with exhaust hoods was developed.

Work is proposed that includes two topics in modeling, one in information retrieval, one on evaluating the effect of the particle size of the SCO, the particle size of the cellulose, the composition of reactants, and the mixture mass on the burn time, and one on the reactivity of liquid chemical oxidizers (LCOs) with cellulosic fuels in open and semi-confined environments. One proposed area in modeling concerns the development of a heat conduction model with internal heat generation for use in subsequent hazard analysis studies, and the other area involves conducting intermediate-scale experiments to provide data to support the validation of hazard assessment models. The proposed information retrieval effort addresses the construction of a reliable data base for use remotely by others to obtain and analyze information on SCOs. The proposed effort on size effect and other parameters on burn time entails the development of models to quantitatively characterize how the burn time depends upon the key parameters for the selected oxidizers.

A review of the existing domestic and international research literature on the physical chemical aspects of ammoniated oxidizers bearing on safety issues should be conducted to help focus on research needs. Such a review and the subsequent research findings would be of value to those concerned with the shipment, handling, and use of solid oxidizers.

***LIST OF SYMBOLS, ABBREVIATIONS, AND UNITS

Latin and Greek Characters

k	thermal conductivity
m_{fuel}	mass of fuel
m_{SCO}	mass of oxidizer
MW_{SCO}	molecular weight of oxidizer
MW_{fuel}	molecular weight of fuel
n	sample size
N	sample size
Δn	change in gaseous moles between products and reactants
Q_T	rate of change of gas volume at temperature T with respect to time
$\hat{Q}_T$	normalized rate of change of gas volume at temperature T with respect to time
t	time
T_{amb}	ambient temperature
T_i	adiabatic flame temperature
V_{hood}	volume of exhaust hood
V_T	Volume of gas at temperature T

α	scalar coefficient, variable, molar coefficient, significance level
β	scalar coefficient, variable, molar coefficient
γ	molar coefficient
δ	molar coefficient
τ	time
$\tau_{O:F}$	burn time for an oxidant-fuel mixture
μ	molar coefficient, mean
σ	molar coefficient, standard deviation, specific heat

ρ density

Mathematical Operation Symbols

$>$ greater than

$<$ less than

$\pm$ plus or minus

$\leq$ less than or equal to

$\geq$ greater than or equal to

Σ summation operator

$\sum_{i=1}^n x_i$ finite summation of terms; $\sum_{i=1}^n x_i = (x_1 + x_2 + x_3 + \dots + x_n)$

$\sum_{i=1}^{\infty} x_i$ infinite summation of terms; $\sum_{i=1}^{\infty} x_i = (x_1 + x_2 + x_3 + \dots + x_i + x_{i+1} + \dots)$

$\int$ integral operator

$\int_a^b$ definite giving limits; **a** is the lower limit, and **b** is the upper limit

$\int_{-\infty}^x p(t)dt$ distribution function, an integral of the probability density function

with the integration variable being t

d ordinary differential operator

O:F oxidizer to fuel mass ratio

X times

Δ increment (change) operator

Abbreviations

ACCESS relational database (Microsoft)

ATSDR Agency for Toxic Substances and Disease Registry

av average

avg average

AWG	American Wire Gage
BP	boiling point
CEA	chemical equilibria applications - relates to NASA Lewis Code
DC	direct current
DRAM	computer memory type
F	fuel
F-distribution	probability distribution function for use with standard deviations
F-test	hypothesis test of standard deviation based on the F-distribution
FORTRAN	programming language for performing computations (formula translation)
HP	Hewlett Packard
http	Internet symbol, hypertext transfer protocol
IARC	International Agency for Research on Cancer, a division of the UN World Health Organization (WHO)
LCO	liquid chemical oxidizer
LINUX	32-bit operating system derived from UNIX for use on PCs
NA	not available
NASA Lewis CEA Code	Software written in FORTRAN and capable of being run under Windows NT with DEC's 32-bit Visual FORTRAN 5.0 compiler for studying chemical equilibria for chemical reactions such as solid oxidizer - fuel ones
NC	not classified
ND	no data
NT	not tested, new technology (one of Microsoft's 32-bit operating systems)
NTP	National Toxicology Program of US Department of Health and Human Services
O	oxidizer
OSHA	Occupational Safety and Health Administration of US Department of Labor
PG	packing group
SCO	solid chemical oxidizer
SCSI	small computer system interface
sd	standard deviation
SD	standard deviation
SQL	structured query language
t-distribution	Gosset's probability distribution function for use with means
t-test	hypothesis test for use with means based on Gosset's student t-distribution
TIGERWIN	Windows based PC code that is frequently used to calculate ideal and nonideal

	thermodynamic properties of an explosive formulation
UNIX	32-bit operating system
WHO	World Health Organization, a division of the United Nations
Wt	weight
www	Internet symbol, world wide web

Units of Measure

a	amperes
cc	cubic centimeters
cm	centimeters (2.54 cm = one inch)
°C	degrees centigrade
°K	degrees Kelvin
kva	kilovolt amperes
L	liters
L/s	liters per second
m	meters
mm	millimeters
μm	micrometers
Ω	ohms
s	seconds (time)
sec	seconds (time)
v	volts
w	watts

***INTRODUCTION

The primary objective of this experimental effort was to evaluate the equivalency of the United Nations' (UN's) newly adopted, solid-oxidizer hazard test with the existing United States (US) test. The UN test procedure for the classification of oxidizing solids (**PR¹ 1, 2**) requires the measurement of the combustion time of a mixture of a solid oxidizer and dry fibrous cellulose with a fiber length between 50 and 250 μm and a mean diameter of 25 μm . The US test method for solid oxidizers (**PR 3**) uses softwood sawdust as the fuel with the particle size being less than 1,600 μm . The type or grade of sawdust is not specified. Because of this ambiguity, the results of the test have varied greatly and sometime have been contradictory. The Department of Transportation (DOT) is interested in classifying solid chemical oxidizers (SCOs) to determine restrictions for shipping SCOs.

Currently the UN test procedure for SCOs calls for a decision on whether or not to grind the SCO. The exact wording in SECTION 34.4.1.2.6 of the UN Manual of Tests and Criteria published as a part of the Recommendations on the TRANSPORT OF DANGEROUS GOODS, second revised edition, is as follows.

34.4.1.2.6 The substance, in the form in which it will be transported, should be inspected for any particles less than 500 μm in diameter. If that powder constitutes more than 10% (mass) of the total, or if the substance is friable, then the whole of the test sample should be ground to a powder before testing to allow for a reduction in particle size during handling and transport.

However, the UN procedure does not define the fineness of ground powder to be used in conducting the classification tests.

The UN Test procedure makes use of potassium bromate as the sole reference SCO and precisely specifies the size cut (150 to 300 μm) to be used in preparing mixtures of the three different ratios of SCO-to-cellulose. For UN classifications, conical shaped piles (30-grams) with mass ratios of

¹ PR denotes published reference listed in the REFERENCE section of the report.

SCO to cellulose of 1:1 and 4:1 are each ignited by an inert metal (Nichrome) wire which is heated at 150 watts and applied through out the test near a low-heat-conducting refractory surface. The UN burn time is measured from the application of heat to the cessation of combustion for the main body of the mixture.

The UN test procedure for SCOs specifies dry fibrous cellulose as the fuel. The cellulose specified is more uniform in consistency than sawdust which possesses properties dependent on many natural variables. Replications of each mixture burn with the sample size being five are specified to determine a mean burning time. These mean burning times are compared to different reference mass ratios of KBrO_3 mixed with cellulose. The KBrO_3 is specified to have a particle size range of 150 to 300 μm . Classification in Packing Group (PG) III requires that the mean burning time of each SCO mass ratio, 1:1 and 4:1, be equal to or less than the mean burning time of a 3:7 mass ratio of KBrO_3 mixed with cellulose. Classification in Packing Group II requires that the mean burning time of each SCO mass ratio, 1:1 and 4:1, be equal to or less than the mean burning time of a 2:3 mass ratio for KBrO_3 . Classification in Packing Group I (most hazardous) requires that the mean burning time of each SCO mass ratio, 1:1 and 4:1, be equal to or less than the mean burning time of a 3:2 mass ratio for KBrO_3 . Although the UN procedure does not specify the particulate size of SCO to be used in classification studies, this investigation included the use of SCOs with the particle size being just under 300 μm in order to facilitate a comparison of the US and UN procedures.

The UN procedure specifies KBrO_3 as the only reference SCO. KBrO_3 is listed in group 2B of a list compiled by the International Agency for Research on Cancer (IARC). This group contains the names of chemicals that have shown evidence of causing cancer in animal studies and are considered to be possibly carcinogenic to humans. The IARC was established in 1965 by the World Health Organization. The IARC's mission under the umbrella of the United Nations is to coordinate and conduct research on the causes of human cancer and to develop scientific strategies for cancer control. Various lists of carcinogens are posted on the web site of the College of Science of the Texas A&M University <(IR² 1)

² IR denotes Internet Reference URL listed in the REFERENCE section of the report.

<http://joy.tamu.edu/nanweb/carcinogens.html> > . The site's carcinogen postings include: IARC's, the US Department of Health and Human Services' National Toxicology Program's (NTP's) list, and OSHA's list. The NTP and OSHA lists do not include potassium bromate. The Food and Drug Administration has been underway since at least 1996 with a determination study on potassium bromate as a carcinogen. In 1990, under Proposition 65, "The Safe Drinking Water and Toxic Enforcement Act of 1986", the State of California listed potassium bromate as a chemical known to the State to cause cancer. Special precautions are therefore needed to safely handle KBrO_3 .

Presently the US test procedure involves mixing samples of each SCO that will pass through a sieve mesh size of 300 μm with softwood sawdust that will pass through a sieve mesh size smaller than 1,600 μm . For US classifications, conical shaped piles with mass ratios of SCO to sawdust of 1:1 and 4:1 are each ignited by a circular ignition wire (whose bare wire temperature is 1,000 °C with the power being terminated once combustion gets underway) placed near a low-heat-conducting refractory surface. The US burn time is measured from the visual onset of combustion (open flaming or smoking) during the application of heat to the cessation of combustion for the main body of the mixture. For the US tests the time of burning is recorded for each mixture. The test is repeated two more times for each mass ratio. The mean burning times for each three-test set are calculated and compared with each mean burning time for a 1:1 mass ratio of sawdust with each of three reference SCOs; ammonium persulfate, $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$, potassium perchlorate $[\text{KClO}_4]$, and potassium bromate $[\text{KBrO}_3]$. If the mean burning time for a SCO and sawdust of either mass ratio is greater than the mean burning time for a 1:1 mass ratio for $(\text{NH}_4)_2\text{S}_2\text{O}_8$, then the SCO is not classified in Class 5, Division 5.1 of the US Code of Federal Regulations (CFR) for the shipment of SCOs. If the mean burning time of a SCO and sawdust of either mass ratio is equal to or less than the mean burning time of 1:1 mass ratio for $(\text{NH}_4)_2\text{S}_2\text{O}_8$ but greater than the mean burning time for the 1:1 mass ratio for KClO_4 , then the SCO is assigned to Packing Group (PG) III of Division 5.1. If either of the mean burning times for a SCO is equal to or less than the mean time for a 1:1 mass ratio for KClO_4 but greater than the mean time for a 1:1 mass ratio of KBrO_3 , then the SCO is assigned to Packing Group II. If either of the mean burning times for a SCO is equal to or less than the

mean time for a 1:1 mass ratio for KBrO_3 , then the SCO is assigned to Packing Group I.

In conducting a SCO classification test, it is conceivable that the result of using a SCO powder having a particle size distribution with a small mean size could be a shift in the SCO's Packing Group assignment to a more hazardous classification than would typically occur. This possibility is underscored in the case of ammonium perchlorate (NH_4ClO_4). Coarse NH_4ClO_4 has a Packing Group classification of II. When NH_4ClO_4 particles are extremely small, however, NH_4ClO_4 falls into the explosives category. As noted by (PR 4) Dr. Tadeuz Urbański of the Warsaw Politechnika University in his book, Chemistry and Technology of Explosives, Vol II, published by Pergamon Press, 1965 - "Ammonium perchlorate explodes under the impact of a 10-kg weight dropped from a height of 15 cm." Its sensitivity is about six times less than that of ammonium chlorate. Professor Urbański notes that "Ammonium chlorate is sensitive to impact: it explodes if a 2-kg weight is dropped on it from a height of 15-20 cm." Some researchers have suggested that NH_4ClO_4 will detonate when the particle size is less 45 μm . According to the UN Manual of Tests and Criteria, 2nd revised edition, when ammonium perchlorate of 45 μm size is subjected to the **Internal Ignition Test** in a 45-mm diameter "pipe", it causes destruction of the vessel, indicating the substance undergoes transition from deflagration to detonation (see page 45 of PR 2). Ammonium perchlorate is extensively used in solid propellant systems. It is of great commercial value and is in great demand.

Because all the SCOs are extremely reactive, all are irritants, some are corrosive, some are extremely toxic, and some are carcinogenic, and because some of the combustion products are toxic and some of the reactions are extremely rapid, the samples are prepared in an exhaust hood and the combustion process carried out in the hood. A fume extraction system is advised as noted in the UN test procedure (PR 2). When particulates are entrained by an energetic flame, it is essential that respirators and safety goggles be used for the reaction might in some laboratory situations overwhelm the hood's capability to contain it. When a violent combustion reaction is conducted and the exhaust hood is overwhelmed, some of the deposited debris that has not been removed from past studies can become entrained and can be ejected out into the laboratory work area. Thus, consideration has to be given in

advance as what kind of a hood arrangement and procedures should be employed to minimize laboratory contamination.

Solid Oxidizer - Fuel Reactions and Their Characterization

Solid oxidizer - fuel reactions are most important to our economy, space research, and the military. Solid oxidizers are widely used in the chemical processing industry, construction industry, explosives, pulp and paper manufacturing, and in mining. Many terms are used to describe reactions between oxidizers and fuels. The associated terminology involves terms such as burning, combustion, deflagration, and detonation. [The Glossary section provides a detailed discussion of this associated terminology.] The reaction between a solid oxidizer and a fuel is complex. It is a heterogeneous reaction, involving surface decomposition and gas phase reactions with energy and mass transport. There are often many different reaction mechanisms to characterize the combustion process. Through the use of thermochemical calculations based on the free energy/chemical equilibria concept, the adiabatic flame temperature for the reaction and chemical composition of the reaction products can be computed. Using minimum energy techniques, one can rule out some mechanisms as being unlikely. The NASA Lewis Chemical Equilibrium with Applications (CEA) Program with supporting codes (PR-5, 6, 7, 8)³, written in ANSI standard FORTRAN 77 and capable of being run under Windows NT with DEC's 32-bit Visual FORTRAN 5.0 compiler, is a popular one for studying chemical equilibria associated with solid oxidizer/fuel combustion reactions. TIGERWIN, version 4.0, is a Windows based PC code that is frequently used to calculate ideal and nonideal thermodynamic properties of an explosive formulation. It allows the use of various equations of state. It is marketed by Blasting Analysis, Inc. in Allentown, PA.

The understanding of hazard analyses associated with solid oxidizers is often steeped in physical

³ In PR 5, the authors state the various assumptions on which the calculations are based and analyze the appropriate equations and methods for their solution. The equations describe the conditions for chemical equilibrium. Applications to rocket performance, shocks, and detonations are also described. In PR 6, the authors present: (1) the details for preparing data sets, (2) description of output tables, (3) an account of the overall modular organization of the program and directions for making modifications, (4) description of the function of each subroutine, (5) list of error messages and their significance, and (6) a number of application examples. In PR 7, the author documents the new transport property data that will be used in the CEA program in its update. The program is commercially available.

chemistry. Oxidizers are combined with fuels to form explosives and blasting agents. Carbon and hydrogen are two common fuels. Although water contains hydrogen and oxygen, it is not an oxidizer - it is often an end product in a combustion process. In an explosive the fuel and oxidizer can be together in one molecule, called a "molecular" explosive, e.g., nitroglycerin or very fine ammonium perchlorate, or combined as two or more components. Ammonium nitrate because of its insensitivity in pure state, for transportation purposes, is classified as an oxidizer even though it contains four hydrogen atoms and three oxygen atoms. Were ammonium nitrate to burn, two molecules of it would give one molecule of nitrogen and four water molecules with one oxygen molecule left over. To make it effective as an explosive, additional fuel is added to use up the oxygen - this is known as oxygen balancing. Adding a slight amount of fuel makes it more sensitive. The most common fuel additive used with ammonium nitrate is fuel oil; the combination is referred to as ANFO. By varying the type of fuel added to ammonium nitrate, its sensitivity can be changed drastically.

Although ammonium nitrate is an excellent blasting agent and has been used safely in blasting operations, there have been unfortunate accidents associated with ammonium nitrate. An account of some of these mishaps has been published recently in *The Journal of Explosives Engineering* in an article entitled "*Dispelling Some of the Myths About Ammonium Nitrate*" by Professor Paul Worsey and Brandon Weeks in (PR 9) to which Robert Hopler (the author of the continuing series entitled "*Explosives 100 Years Ago*" appearing in the same journal) responded (PR 10) in a correcting manner in his "Letter to the Editor" in the subsequent issue. Some interesting comments on these mishaps have been contributed by Worsey, Weeks, and Hopler. The comments are presented below with those of Hopler, taking issue with those of Worsey and Weeks; Hopler's comments directly follow those of Worsey and Weeks.

WORSEY AND WEEKS: "A number of disasters led up to the modern use of ANFO, dating back at least as far as 1916 when an ammonium nitrate evaporation and crystallization plant exploded in Gibbstown, NJ. The first major disaster occurred in

Oppau, Germany in 1921 when permissible explosive charges were used to break up piles of caked ammonium nitrate. An estimated 9,900 short tons detonated destroying 75 percent of the buildings in Oppau. Five hundred and sixty people were killed, including three people in Mannheim at a distance of four miles from the explosion. Strangely, until Oppau, ammonium nitrate was considered to have no explosion hazard”.

HOPLER: “The explosion in Oppau, Germany was of approximately 4500 tons (not 9,900 as stated) of a fertilizer which was a double salt of ammonium nitrate and ammonium sulphate (not ammonium nitrate alone). It was well known at the time that ammonium nitrate by itself was explosive, but the double salt had never exhibited such tendencies. As many as 20,000 blasts with dynamite (whether it was ‘permissible dynamite’ is unknown) had been made over many years to break up caked piles, without mishap. Just prior to the day of the explosion, a large increase in production rate was ordered, hotter material than normal was placed on the pile, and workers were complaining of noxious fumes from the storage piles. The official report of the accident in 1923 gave the opinion that the explosion was probably due to a spontaneous reaction in the material. There were no survivors to testify that explosives were even being used in that instance. However, the use of explosives ceased as a further safety measure.”

WORSEY AND WEEKS: “The largest non-war time disaster to occur in the United States was caused by ammonium nitrate on April 16-17, 1947 at Texas City, Texas. Two Liberty ships the Grandcamp and the High Flyer were loaded with 3,340 tons of ammonium nitrate that was coated with petroleum rosin. At 8:10 a.m. smoke was detected in the hold of the Grandcamp. An hour later a catastrophic explosion occurred. Embers ignited cargo on the High Flyer, which subsequently exploded at 1:10 a.m. the next morning. When the chaos had ended, 600 people had lost their lives. The Texas City disaster triggered adoption of controls on ammonium nitrate storage, handling, and transportation. However, the United States has never required that fertilizer grade ammonium nitrate be mixed with a material that will render it non-explosive. Some European countries require that fertilizer grade ammonium nitrate be mixed with limestone or dolomite.”

HOPLER: “The mixtures with limestone, etc., were introduced to combat terrorism, and have been almost totally ineffective in that regard. It has been proven that the addition of

inert materials at the legislated 21 % by weight does not make ammonium nitrate unsuitable as an explosive."

In 1988 a devastating explosion occurred at an ammonium perchlorate plant owned by Pacific Engineering Production Company (PEPCON) at Henderson, Nevada, resulting in massive destruction and loss of life.

Obviously with ammoniated solid oxidizers (such as the nitrate and perchlorate ones), disasters have occurred that have caused great destruction and/or loss of life. It is unfortunate and distressing that even after more than 50 years there is still (1) a lack of understanding of what actually caused some of these disasters and (2) a vague description of the actual chain of physical chemical events that took place. This great potential for disaster and the apparent lack of understanding of the physical chemical processes associated with ammoniated solid inorganic oxidizers underscore the need for additional fundamental research on solid oxidizers and their reactions with fuels.

Clearly, a better understanding of the physical chemical aspects is needed to prevent disasters involving the shipment, storage, handling, and use of ammoniated oxidizers. The specific physical chemical research topics that need to be pursued include:

1. The particle size-sensitivity relations for various stimuli and decomposition processes for ammoniated oxidizers;
2. The reaction processes and kinetics associated with binary oxidizers that include at least one ammoniated SCO in each system;
3. The reaction processes and kinetics for ammoniated oxidizers mixed with activators or deactivators;
4. The "critical mass" determination and associated stimuli for explosive like behavior of ammoniated oxidizers;
5. The contamination of ammoniated oxidizers with fuel during storage and shipment; and
6. The spontaneous heating of ammoniated oxidizers in storage (with identification of the

likely range of ambient temperatures).

A review of the existing domestic and international research literature on the physical chemical aspects of ammoniated oxidizers bearing on safety issues should be conducted to help focus on research needs. Such a review and the subsequent research findings would be of value to those concerned with the shipment, handling, and use of solid oxidizers.

*****EQUIPMENT, SOURCES OF CHEMICALS, AND EXPERIMENTAL PROCEDURE**

Equipment

Two laboratory exhaust hoods, located in restricted areas, were used in the testing of the SCOs. The first hood, located in Building 29 of the Pittsburgh Research Laboratory (PRL) was constructed of stainless steel and had an internal volume of about 790 L. The second hood located in Building 126 was older and lined with Transite®. Its volume was about 819 L. The air velocities and pressure drops of air flowing into the hoods, measured at 23° C, are shown in Appendix A.

Other key items of equipment included:

- DC power supply (HP 6261B 0-20 v and 0-50 a) and Variac (2.8 kva and 20 a)
- Retsch grinding mill (stainless steel construction), food processor for pulverizing SCOs, and mortar and pestle
- Sieves
- Drying ovens, convection type, 65 °C and 105 ° C
- Portable balance
- Desiccator cabinets
- Respirators (for particulates and acid gas), safety goggles, rubber aprons
- Video camera, recorder, monitor, and stop watches
- Stainless steel trays to control laboratory contamination and porcelain tray (about 40 cm by 70 cm by 5 cm) to help contain the debris generated during the combustion process

The Hewlett Packard DC power supply that was used in the laboratory in Building 29 essentially eliminated the drift problem with current that is associated with ac variable transformers. A Variac to which a 30-amp ac ammeter was connected in series was used in conducting the work in Building 126. Having ammeters on both power supplies enabled the experimentalists to confirm continuity before forming the conical pile and monitor the application of power during heating. This enabled one to easily detect a break in the heater wire in the middle of a test.

Chemicals

Vendors and catalog numbers for chemicals tested are listed in table 1.

Table 1.--Chemical substances and sources of supply

Item No.	Chemical	Formula	Vendor	Catalog No.
1	Ammonium nitrate	NH_4NO_3	Fisher Scientific	A676-500
2	Ammonium perchlorate	NH_4ClO_4	Aldrich Chemicals	20,850-7
3	Ammonium persulfate	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	Aldrich Chemicals	21,558-9
4	Calcium hypochlorite	$\text{Ca}(\text{ClO})_2$	Fisher Scientific	C100-500
5	Calcium nitrate tetrahydrate	$\text{Ca}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$	Fisher Scientific	C109-500
6	Cerium ammonium nitrate	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	Fisher Scientific	C248-500
7	Magnesium perchlorate	$\text{Mg}(\text{ClO}_4)_2$	Fisher Scientific	M54-500
8	Potassium bromate	KBrO_3	Fisher Scientific	P207-500
9	Potassium chlorate	KClO_3	Fisher Scientific	P210-500 & P212-500
10	Potassium nitrate	KNO_3	Fisher Scientific	P261-3
11	Potassium nitrite	KNO_2	Fisher Scientific	P267-250
12	Potassium perchlorate	KClO_4	Aldrich Chemicals	21,558-9

13	Potassium periodate	KIO_4	Fisher Scientific	P277-100
14	Potassium permanganate	KMnO_4	Fisher Scientific	P279-500
15	Sodium chlorate	NaClO_3	Fisher Scientific	S268-500
16	Sodium nitrate	NaNO_3	Fisher Scientific	S343-500
17	Sodium perchlorate monohydrate	$\text{NaClO}_4 \cdot \text{H}_2\text{O}$	Fisher Scientific	S490-500
18	Sodium peroxide	Na_2O_2	Fisher Scientific	S363-500
19	Cellulose (125 μm , ave. size)	$(\text{C}_6\text{H}_{10}\text{O}_5)_x$	Whatman Labsales	CF-11
20	Cellulose (20 μm , ave. size)	$(\text{C}_6\text{H}_{10}\text{O}_5)_x$	Sigma Chemicals	S3504
21	Basswood sawdust	--	Dallison Lumber Co., Jacksonburg, WV	--
22	Yellow pine	--	NIOSH PRL stock	--
23	Wood flour	--	NIOSH PRL stock	--

The experimental hazards that can be encountered when working with some of the above chemicals are discussed in Appendix B.

Experimental Procedure

A brief summary of the main steps in the experimental procedure for conducting the SCO tests is listed below. A more detailed listing of the steps in the procedure can be found in Appendix C.

1. Put on personal protective equipment.
2. Make sure hood ventilation is functional.
3. Prepare SCOs and fuels in the hood for drying.
4. Place SCOs and fuels in separate drying ovens.
5. Weigh out dried samples in the hood and store them in separate desiccators.
6. Prepare an ignition wire, place wire on Fiberfrax refractory pad, and adjust value of electrical current. (Respirators and gloves need to be worn when cutting and handling

Fiberfrax refractory sheets.)

7. Prepare test mixtures of SCOs and fuels in the hood.
8. Form conical pile of mixture on top of the heating wire.
9. Enter test conditions in a laboratory notebook.
10. Set two stopwatches and start a video camera recording with the timing caption visible.
11. Start the electrical current to the heating wire and the stopwatches simultaneously.
12. When flaming starts, stop one of the stopwatches.
13. When flaming stops, stop the other stopwatch.
14. Review video tape recording to verify burning-time interval and record times.
15. Clean inside area of hood.
16. Clean personal protective equipment.

To facilitate the collection of data, a data base record form was developed. It is presented in Appendix D. This form also provides the structure for entering test data in a computerized data base.

The SCOs were reduced in size by using various pieces of equipment. These included mortar and pestle, Cusinart food grinding mill, and Retsch grinding mill distributed by the Brinkmann Company. A Cusinart mill whose blades had experienced wear would not pulverize the "hard" sodium peroxide beads. When a new food processing unit was used, the sharp blades were able to breakup the peroxide beads. Particle size distribution ranges for SCOs were acquired using stainless steel sieves. The sawdust used was passed through a 1.6 mm sieve. Except for the hygroscopic SCOs [KNO_2 and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$], the SCOs were dried in a convection oven heated to 65° C. The wood flour, basswood sawdust, and cellulose powder were dried in another oven heated to 105° C. The dried SCOs and fuels were stored in separate desiccators. Prior to conducting tests, the SCOs and fuel were weighed in small paper cups on a portable balance accurate to 0.1 g and shaken together in a closed cardboard container (of volume of one liter and of cylindrical shape) or stirred with a wooden tongue depressors in a large paper cup (of volume of about 500 cc) for approximately one minute. (Tests with longer mixing times were conducted to evaluate the adequacy of mixing, and one minute of vigorous mixing was found

to be adequate.)

To avoid destructive pitting of a refractory material and provide a clean surface for each burn test, 10-cm square sheets of Fiberfrax (ceramic blanket) about 4 mm in thickness were placed on top of the rigid refractory material and used as disposable burn surfaces.

To characterize the surface temperature of the heating wire as a function of the electrical current, optical pyrometry measurements were recorded. The heating wire selected for conducting the classification and reference standard tests was of American Wire Gage (AWG) -18 size, had a composition of 80% Ni and 20% Cr, and was heated by 150 w to an open air temperature of 1,000° C using either a Variac or a direct current power supply.

The UN procedure (PR 2) called for use of a special inert metal (Nichrome heating wire) in an "indented" open circle configuration of particular resistance [$6.0 \pm 0.5 \Omega/\text{m}$, diameter [$0.6 \pm 0.05 \text{ mm}$], and length [$30 \pm 1 \text{ cm}$] being heated by $150 \pm 7 \text{ w}$, use of a conical mold [funnel of 60° with a base diameter of 70 mm] with the small end sealed for forming the 30-gram pile, low thermal conductivity surface ($0.23 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 0°C) for holding the mixture pile, air flow rate 0.5 m/s or less by the pile, and standards prepared from oxidizers in the 150 to 300 μm particle size range. The UN procedure called for using dried fibrous cellulose, with a fiber length between 50 and 250 μm and a mean diameter of 25 μm . The UN procedure called for the timing of the combustion process to start when the power to the wire was first applied and with the power applied continuously during the combustion process.

The US (PR 3) procedure called for the particle size of the solid oxidizer to be classified to be less than 300 μm and the softwood sawdust to be less than 1,600 μm with the heater wire in an open circle configuration having a "bare" [in air] temperature of 1,000 °C. The power to the wire should be turned off just after the onset of burning, and the timing of the combustion process should start at the first sign of combustion. Both test procedures called for well mixed mixtures of oxidizer and fuel.

Because of (1) difficulties in acquiring the specified heating wire for the UN tests, (2) the problem of maintaining the wire one mm above the support base, and (3) the problem of keeping the combustion fumes within the exhaust hood, there was a need to determine what elements were crucial in the

procedure. Therefore, an analysis was made of how critical the specific test configuration requirements were. What was considered to be crucial were:

1. The 150 wattage applied in the UN tests and the 1,000 °C wire temperature in the US tests,
2. A 30-gram mixture size,
3. Process of handling of SCO samples
 - Drying hygroscopic materials in a convection oven fed with ambient air created agglomeration;
 - Drying some of those having a high amount water of hydration converted the solid to a liquid state;
 - Drying certain chemical such as $\text{Mg}(\text{ClO}_4)_2$ or $\text{Ca}(\text{ClO})_2$ for extended periods of time at 65°C in a convection oven resulted in their degradation as oxidizers,
4. Heater wire length and configuration for both US and UN tests,
5. Start of the timing of the combustion process at the onset of heating in the UN tests and just after the first sign of combustion in the US tests,
6. Complete mixing of the SCO and fuel component, and
7. The decision criteria for determining the cessation of open flaming, or smoking in the absence of open flaming.

The precise shape of the wire was not considered to be crucial as long as a conical or parabolic pile configuration was used that covered the heating wire. There was a wide range in bulk densities for the mixtures (with corresponding wide range in volumes) and thus an obvious need to avoid compacting the mixtures. It was decided after numerous tests that a free flow of the mixture to form a pile at its natural angle of repose did not adversely affect matters and greatly simplified the work effort. The precise diameter of the heater wire was not as crucial as the power input to and the temperature of the wire of fixed length. Four different wire diameters were examined in tests. For the UN tests it was

decided that it was better to have a wire that would not readily break in the middle of the burn process. In comparing the burn processes between the US and UN tests it was felt that the same diameter and wire resistance should be used. Consequently, the No.18 AWG (thickest of the four wires) was selected. To (1) facilitate conducting the tests, (2) help in the cleanup after a test, and (3) provide better uniformity in controlling conduction losses to the support medium, disposable thin, porous sheets of Fiberfrax were placed on top of the low conducting support board beneath the mixture pile. In all but the Na_2O_2 tests, a single sheet was used. The reaction of the sodium peroxide was thermally intense that up to four layers of Fiberfrax were needed to stop the penetration.

In order to make sense out of burn times, it was decided that in the case of burns with open flaming that cessation of open flaming should exclude outlying mini-piles and be determined just when the main body of the flame diminished (sometimes noted with the changing of the flame color from yellow to blue) to a relatively low value for particular mixture. When no open flaming occurred to mark the duration of combustion, it was decided that the cessation of smoking should be determined just when the main volume of smoke diminished to a relatively low value for the particular mixture. Admittedly, it represents a rather subjective criterion.

The particle size range of the mixture was considered to be of paramount importance. Consequently, tests at different size cuts were conducted to better evaluate size effects. Some SCO samples that easily picked up moisture could not be dried in the convection oven that used ambient air as input - for they would cake and degrade. Some SCO samples that contained water of hydration turned into a liquid upon being heated at 65 °C. Although most oxidizers were dried at 65 °C, there had to be exceptions. Both the cellulose and sawdust were dried at 105 °C.

***RESULTS AND DISCUSSION

Description of Data

Trends in test data can be spotted by viewing the plots of burning times versus oxidizer to fuel ratios. These plots are presented in Appendix E. Because the relationship between burning time and mixture ratio is often nonlinear, curves were not superimposed on the data plots involving just the 1:1 and 4:1 mixture ratios. This nonlinear behavior is depicted in eight plots: (1) KClO_3 - basswood [Figure E-6], (2) KIO_4 -basswood [Figure E-9], (3) KBrO_3 - cellulose [Figure E-25], (4) KBrO_3 -cellulose [Figure E-26], (5) KClO_3 - cellulose [Figure E-27], (6) KClO_4 -cellulose [Figure E-32], (7) KMnO_4 -cellulose [Figure E-35], and (8) NaClO_3 -cellulose [Figure E-36].

In general, as the mixture ratio of oxidizer to fuel increases from 1:1 to 4:1, the mean burn times decrease. However, in the case of the nitrate oxidizers (with one exception - KNO_3) and the periodate oxidizer, there is a decided increase in the burning time as the mixture ratio of oxidizer to fuel increases from 1:1 to 4:1. This definite increasing trend is depicted in the following five plots: (1) KIO_4 -basswood [Figure E-9], (2) NH_4NO_3 -cellulose [Figure E-18], (3) $\text{Ca}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$ -cellulose [Figure E-22], (4) KIO_4 - cellulose [Figure E-33], and (5) NaNO_3 -cellulose [Figure E-37].

The effect of particle size of the oxidizer on the burning time is in many instances a most notable one. Coarse, as shipped oxidizers, were at times tested for comparison with oxidizers having a particle size range of less than 0.30 mm. Often there were great reductions in burning times with a decrease in particle size. Comparing times for Na_2O_2 -basswood [See Figures E-15 and E-16.] gives for the 1:1 mixture approximately a 9.7X reduction factor and for 4:1 a 5.5X reduction factor. Comparing times for $\text{Mg}(\text{ClO}_4)_2$ -cellulose [See Figures E-23 and E-24.] gives for the 1:1 mixture approximately a 2.8X reduction factor and for 4:1 a 1.1X reduction factor. Comparing times for Na_2O_2 -cellulose [See Figures E-39 and E-40.] gives for the 1:1 mixture approximately a 12.9X reduction factor and for 4:1 a 4.3X reduction factor. This size effect is demonstrably shown over a wide range of mixture ratios in the comparison of the KBrO_3 cellulose plots for the 0.15 mm to 0.30 mm size cut and the less than 0.15 mm one [See Figures E-25 and E-26.] Comparing times for KBrO_3 -cellulose [See Figures E-25 and E-26.]

gives for the 1:1 mixture approximately a 2.5X reduction factor, for 4:1 a 1.6X reduction, for the 3:2, a 2.7X reduction, for the 2:3, a 2.8X reduction, and for the 3:7, a 1.6X reduction.

Sets of individual burning times of SCOs with various solid fuels, the means and standard deviations of the sets, and information about the SCO particle sizes are in Appendix F in tables F-1 through F-4. When there were ambiguities or the data were "suspect", the cases were so noted. Over 800 combustion tests were completed. Video tape records were made for about 95 % of all of the tests. Because this report includes almost all of the quantitative data, it, therefore, provides analysts with a better perspective with which to understand the variability in conducting SCO tests. Moreover, it provides a good basis for the subsequent testing of statistical hypotheses. Special attention was given to particle size effects. In many instances SCOs taken from the supplier's bottles were also tested without further size reduction. All suspected outliers were tabulated, thus allowing for future application of various statistical rejection techniques. All the basic "raw" data are provided, so that analysts with spreadsheet data analysis tools can, if they desire, construct least square fits of data for interpolation of burning times as a function of mass ratio of oxidizer to fuel and also obtain the statistical parameters for the "goodness" of the fit.

Table F-1 provides individual burning times, mean burning times, and standard deviations for reference SCOs for both the UN and US procedures. Table F-2 provides individual burning times, mean burning times, and standard deviations for SCOs tested by the UN procedure. Table F-3 provides individual burning times, mean burning times, and standard deviations for SCOs tested by the US procedure. Table F-4 provides individual burning times for SCOs tested with wood flour, yellow pine sawdust, and cellulose for the heating power range of 18 to 140 watts; it also includes the "bare" wire temperature values associated with the power settings based on AWG 24 wire. This data was collected early in the study to perfect laboratory procedures and understand the effect of the power applied to the heating wire on the burning time. Based on the KNO_3 -wood flour data, one can observe that as the power applied decreases below 40 watts there is a significant increase in the mean burning time. (In these tests the power was turned off just after combustion was noticed.) Table F-5 summarizes the data in

tables F-1 through F-3 and compares UN and US burning times for two mass ratios. Examination of Tables F-1, F-2, F-3, and F-5 indicates that generally the standard deviation of the mean burning time is less for the UN procedure than for the US procedure. Out of the 23 possible comparisons of standard deviations, eleven of the UN ones were decidedly less than the US ones, four were approximately the same, and eight UN ones were greater than the US ones. Eight of the standard deviation comparisons were based on the size reduction of the SCO by mortar and pestle. Most likely, hypotheses testing of the means with the t-test would provide more revealing comparisons. (In the study of means the t-test is often used; and in the study of standard deviations the F-test is often used.)

Table G-1 in Appendix G indicates the measured size distributions of SCOs from various vendors. The SCOs from their original shipping containers were tested to compare burning times with the burning times of the ground samples.

It is important to note that the mean measured burning time from the PRL data for the reference 3:2 mass ratio of KBrO_3 to cellulose was considerably greater than the 4 seconds published by the UN (PR 2). We obtained a mean of 14.1 s and a standard deviation of 1.2 seconds for a sample size of seven. When finer KBrO_3 (0-to-150 μm size range) was used, the mean burning time was closer to the UN published value. A mean of 5.3 sec and a standard deviation of 0.8 s were obtained with a sample size of five. This difference in combustion times between that published in the UN document and the value obtained in this research effort for the 3:2 KBrO_3 -to-cellulose mixture underscores a need to do a more extensive study of the effect of SCO particle size on burning times.

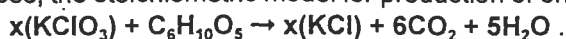
Comparisons of experimental SCO-fuel mass ratios for minimum combustion times and calculated stoichiometric mass ratios are listed in table 2. Although sparse data has been collected for studying the relationship between mean burn times and oxidizer-fuel mass ratio for many of the oxidizers, that which has been collected for some indicates that there exists a pronounced minimum value for the burn time. To unravel the differences between the calculated stoichiometric, more data and information is needed - quite possibly some important parameters are not being controlled in the tests, making it difficult to analyze results. The degree of completion of the reaction and the degree of scattering of unreacted

components during the early stage of the combustion process are difficult to control for conical piles. If the mixtures were spread out in a thin strip and ignited at one end, it might help to better control the combustion parameters. The experimental mass ratios were obtained from the graphs relating mass ratios and burning times that appear in Appendix E. They were calculated based on the assumption that carbon monoxide was not present as a product⁴. A possible reason for most of the experimental mass ratios being less than the stoichiometric mass ratios is the burning time being based on the termination of open flaming. The total reaction would include smoldering following cessation of open flaming. Also to a certain extent, atmospheric oxygen would be present in the voids of the mixture which would augment the oxygen from the SCO. This slight excess of oxygen would absorb energy and tend to slow the reaction rate. If the experimental mass ratio of oxidizer to fuel is less than the stoichiometric mass ratio, oxygen to complete the combustion must travel from the ambient air into the void spaces of the pile which in turn would promote a slower reaction rate.

Table 2.--Comparison of experimental SCO-fuel mass ratios for minimum combustion times and calculated stoichiometric SCO-fuel ratios.

Item	SCO & Fuel Mixture	O:F, Experimental	O:F, Stoichiometric Model
1	KBrO ₃ & Cellulose	4.0	4.1

EXAMPLE CALCULATION OF STOICHIOMETRIC MASS RATIO OF KClO₃ TO CELLULOSE: The formula for the cellulose monomer is C₆H₁₀O₅ as given in the 54th edition of the Handbook of Chemistry and Physics published by the Chemical Rubber Company Press. The chemical reaction model that is postulated and balanced for the SCO-cellulose system assumes that all the carbon goes to carbon dioxide because of an excess of oxygen. If x are the moles of KClO₃ that react with ONE mole of cellulose, the stoichiometric model for production of only potassium chloride, carbon dioxide, and water is



Making an oxygen mass balance yields the equation,

$$3x + 5 = 12 + 5, \quad \text{which has the solution, } x = 4.$$

Calculating the mass ratio of potassium chlorate to cellulose yields

$$\text{O/F} = 4[39.1 + 35.5 + 3(16)]/[6(12) + 10(1) + 5(16)] = 490.4/162 = 3.027.$$

If the total mass is 30 g and y is fraction of sum of gram-molecular weights that equals 30 g, then

$$y = 30/(490.4 + 162), \text{ or } y = 0.046.$$

The KClO₃ component in a 30-g stoichiometric mixture is

$$y(490.4) = 0.046(490.4) = 22.55 \text{ g.}$$

The cellulose component in a 30-g stoichiometric mixture is

$$y(162) = 0.046(162) = 7.45 \text{ g.}$$

2	KClO ₃ & Cellulose	2.0	3.0
3	KIO ₃ & Cellulose	NT	5.3
4	KClO ₄ & Cellulose	3.0	2.6
5	KIO ₄ & Basswood	2.0	¹ 4.3
6	KMnO ₄ & Cellulose	6.0	² 7.8
7	NaClO ₃ & Cellulose	3.0	2.6
8	Na ₂ O ₂ & Cellulose	ND	5.8
9	(NH ₄) ₂ S ₂ O ₈ & Cellulose	ND	6.3

NT means not tested.

ND means not sufficient data to determine a minimum combustion time.

¹ For model, basswood was assumed to be all cellulose.

² Ratio assumes MnO₂ is only oxide formed.

Packing Group Classifications

The published UN and US packing group assignments for various SCOs are presented in table 3.

Table 3.--SCOs and packing groups determined from UN and US DOT data

SCO	UN Packing Group ¹	UN Packing Group ²	US Packing Group ³
NH_4NO_3	III		III
NH_4ClO_4	II		II
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	III		III
$\text{Ca}(\text{ClO})_2$	II		II
$\text{Ca}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$	NC ⁴	Not in Division 5.1 ⁵	NC
$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	NC	II	NC
$\text{Mg}(\text{ClO}_4)_2$	II		II
KBrO_3	II		II
KClO_3	II		II
KNO_3	III		III
KNO_2	II		II
KClO_4	II		II
KIO_4	NC		NC
KMnO_4	II		II
NaClO_3	II		II
NaClO_4	II		II
NaNO_3	III	II	III
Na_2O_2	I		I

1. Published Reference 1 .

2. Published Reference 2.

3. Published Reference 3 (CFR).

4. NC means not classified.

5. Not Division 5.1 means SCO is less reactive than SCOs in PG III.

Packing group classifications, based on the UN test procedure, PRL experimental data, and UN published example burning times are listed in table 4 below. UN published (PR 2) example burning times of 100 seconds, 54 seconds, and 4 seconds yielded 30 out of 38 classifications (79 %) as being the same as the published UN classifications. Six of the "DISAGREEMENT" cases were associated with nitrates; one "DISAGREEMENT" was found with a very coarse sample of sodium peroxide; and the remaining "DISAGREEMENT", a border-line case, might possibly be attributed to the potassium chlorate being too finely ground with the mortar and pestle.

Based on our experimental data, to achieve a 100-s burning time for the 3:7 KBrO_3 - cellulose mixture, one must use KBrO_3 coarser than that of the 0.15 mm to 0.3 mm particle size range. To achieve a 54-s burning time for the 2:3 KBrO_3 -cellulose mixture, one can use KBrO_3 in the 0.15 mm to 0.3 mm particle size range. To achieve a 4-s burning time for the 3:2 KBrO_3 -cellulose mixture, one can use KBrO_3 of the 0 mm to 0.15 mm particle size range.

Table 4.--UN SCO packing group assignments determined from NIOSH PRL experimental data and UN published example burning times for KBrO_3

SCO	Size μm	UN, SCO/Fuel								
		1:1			4:1			PG		
		av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
NH_4NO_3	M&P	75	5	5	166	16	5	III	III	✓
NH_4ClO_4	<300	38	8	5	16.7	2.3	5	II	II	✓
	<300	46	4	6	15.7	2.0	5	II	II	✓
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	M&P	NA			NA			III		
	Bottle	NA			>180	--	2	III		
$\text{Ca}(\text{ClO})_2$	M&P	82	11	5	8.7	0.8	5	II	II	✓
	<300	Susp ect			6.0	0.7	5	II		
	<300	Susp ect			5.7	1.0	5	II		
	Bottle	60	6	5	26.8	4.5	5	II	II	✓
$\text{Ca}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$	<300	84	22	5	152	7	4	had been NC (revised as Not in Division 5.1)	III	DISAGREEMENT
	<300	73	8	3	152	11	2	had been NC (revised as Not in Division 5.1)	III	DISAGREEMENT

		UN, SCO/Fuel								
	Size	1:1			4:1			PG		
SCO	µm	av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
	Bottle	138	14	2	136	14	3	had been NC (revised as Not in Division 5.1)	Not in 5.1	✓
(NH ₄) ₂ Ce(NO ₃) ₆	<300	25	5	5	7.4	0.6	5	had been NC (revised as II)	II	✓
	<300	25	4	5	8.1	0.7	5	had been NC (revised as II)	II	✓
Mg(ClO ₄) ₂	M&P	15.3	1.8	5	7.4	1.5	5	II	II	✓
	<300	11.9	1.4	4	8.7	0.7	5	II	II	✓
	<300	11.3	1.4	5	10.6	0.8	5	II	II	✓
	Bottle	44.2	17.3	5	12.1	5.3	4	II	II	✓
	Bottle	21.6	6.7	5	8.6	1.3	5	II	II	✓
KBrO ₃	M&P	22.0	2.1	5	NA			II		
	<150	8.7	2.3	5	4.1	0.5	5	II	II	✓
	>150 and <300	22	2.1	5	6.7	0.9	5	II	II	✓
	<300	NA			NA			II		
KClO ₃	M&P	7.9	0.7	5	4.0	0.7	4	II	I	DISAGREEMENT
	<300	NA			5.7	0.3	3	II		

		UN, SCO/Fuel								
	Size	1:1			4:1			PG		
SCO	μm	av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
	Bottle	8.1	0.4	5	5.8	0.7	5	II	II	✓
KNO ₃	M&P	22	3	5	21	2	5	III	II	DISAGREEMENT
	M&P	26	2	5	13	0.0	5	III	II	DISAGREEMENT
	<300	12	1.0	5	10	0.0	5	III	II	DISAGREEMENT
	<300	12	1.0	5	10	1.0	5	III	II	DISAGREEMENT
KNO ₂	<300	NA			NA			II		
	Bottle	35	2	5	12.7	1.1	5	II	II	✓
KClO ₄	M&P	43	7	5	12.1	1.3	5	II	II	✓
	<104	36.0	5.1	5	14.4	2.3	5	II	II	✓
	<104	34.3	7.5	5	13.6	0.8	5	II	II	✓
KIO ₄	<300	5.9	0.3	4	6.1	0.4	5	NC	II	
KMnO ₄	<300	13.9	0.7	5	6.2	0.2	5	II	II	✓
	<300	14.0	0.7	5	6.5	0.5	5	II	II	✓
	Bottle	21.0	0.7	5	11.7	1.3	6	II	II	✓
NaClO ₃	<300	8.3	1.4	5	5.7	0.6	5	II	II	✓
	Bottle	10.8	3.7	2	5.8	0.0	1	II	II	✓

		UN, SCO/Fuel								
	Size	1:1			4:1			PG		
SCO	µm	av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
NaNO ₃	<300	22.2	1.5	5	31.6	6.2	5	had been III (revised as II)	II	✓
	<300	23.5	3.1	5	30.4	3.3	5	had been III (revised as II)	II	✓
NaClO ₄ ·H ₂ O	<300	23	3	5	11.6	0.4	5	II	II	✓
	Bottle	51	5	4	29	3.0	4	II	II	✓
Na ₂ O ₂	<300	1.7	0.2	3	2.1	0.9	3	I	I	✓
	Bottle	22	2	7	9	2	5	I	II	DISAGREEMENT

µm = micrometers.

av = average burning time of set of n burning times.

sd = standard deviation of set of n burning times.

n = number of burn tests in set.

s = seconds.

Times of burning used to determine above UN Packing Group assignments:

PG I: Less than or equal to 4 seconds [UN published example value for KBrO₃ / Cellulose at 3:2].

PG II: Greater than 4 seconds but less than or equal to 54 seconds [UN published example value for KBrO₃ / Cellulose at 2:3].

PG III: Greater than 54 seconds but less than or equal to 100 seconds [UN published example value for KBrO₃ / Cellulose at 3:7].

Not in Division 5.1: Greater than 100 seconds.

If the PG inferences from test results with 1:1 and 4:1 data differ, then the PG assignment is to the lower PG value of those inferred from the 1:1 and 4:1 test results.

Packing group classifications, based on the UN test procedure and PRL experimental data using potassium bromate in the particle size range of 150 μm to 300 μm , are listed in table 5. The reference mixture, having a 3:2 mass ratio of KBrO_3 to cellulose with a SCO particle size range of 150 μm to 300 μm , when burned yielded a mean burning time 10 seconds greater than the UN published example value. Possibly because of this difference in mean burning time, classifications using the UN KBrO_3 reference standard with a particle size range of 150 μm to 300 μm yielded only 11 out of 38 classifications (29 %) as being the same as the published UN ones. Most of the "DISAGREEMENT" cases are associated with the long burning time associated with the 3:2 mixture of potassium bromate / cellulose, made from 150 to 300 μm KBrO_3 .

Table 5.--UN SCO packing group assignments determined from NIOSH PRL experimental data with 150 to 300 μm particle size for KBrO_3

		UN, SCO/Fuel								
	Size	1:1			4:1			PG		
SCO	μm	av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
NH_4NO_3	M&P	75	5	5	166	16	5	III	III	✓
NH_4ClO_4	<300	38	8	5	16.7	2.3	5	II	II	✓
	<300	46	4	6	15.7	2.0	5	II	II	✓
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	M&P	NA			NA			III		
	Bottle	NA			>180	--	2	III		
$\text{Ca}(\text{ClO})_2$	M&P	82	11	5	8.7	0.8	5	II	I	DISAGREEMENT
	<300	Suspect			6.0	0.7	5	II		
	<300	Suspect			5.7	1.0	5	II		
	Bottle	60	6	5	26.8	4.5	5	II	II	✓
$\text{Ca}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$	<300	84	22	5	152	7	4	had been NC (revised as Not in 5.1)	III	DISAGREEMENT
	<300	73	8	3	152	11	2	had been NC (revised as Not in 5.1)	III	DISAGREEMENT

		UN, SCO/Fuel								
	Size	1:1			4:1			PG		
SCO	µm	av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
	Bottle	138	14	2	136	14	3	had been NC (revised as Not in 5.1)	Not in 5.1	✓
(NH ₄) ₂ Ce(NO ₃) ₆	<300	25	5	5	7.4	0.6	5	had been NC (revised as II)	I	DISAGREEMENT
	<300	25	4	5	8.1	0.7	5	had been NC (revised as II)	I	DISAGREEMENT
Mg(ClO ₄) ₂	M&P	15.3	1.8	5	7.4	1.5	5	II	I	DISAGREEMENT
	<300	11.9	1.4	4	8.7	0.7	5	II	I	DISAGREEMENT
	<300	11.3	1.4	5	10.6	0.8	5	II	I	DISAGREEMENT
	Bottle	44.2	17.3	5	12.1	5.3	4	II	I	DISAGREEMENT
	Bottle	21.6	6.7	5	8.6	1.3	5	II	I	DISAGREEMENT
KBrO ₃	M&P	22.0	2.1	5	NA			II		
	<150	8.7	2.3	5	4.1	0.5	5	II	I	DISAGREEMENT
	>150 and <300	22	2.1	5	6.7	0.9	5	II	I	DISAGREEMENT
	<300	NA			NA			II		
KClO ₃	M&P	7.9	0.7	5	4.0	0.7	4	II	I	DISAGREEMENT

UN, SCO/Fuel										
SCO	Size	1:1			4:1			PG		
	μm	av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
	<300	NA			5.7	0.3	3	II		
	Bottle	8.1	0.4	5	5.8	0.7	5	II	I	DISAGREEMENT
KNO ₃	M&P	22	3	5	21	2	5	III	II	DISAGREEMENT
	M&P	26	2	5	13	0.0	5	III	I	DISAGREEMENT
	<300	12	1.0	5	10	0.0	5	III	I	DISAGREEMENT
	<300	12	1.0	5	10	1.0	5	III	I	DISAGREEMENT
KNO ₂	<300	NA			NA			II		
	Bottle	35	2	5	12.7	1.1	5	II	I	DISAGREEMENT
KClO ₄	M&P	43	7	5	12.1	1.3	5	II	I	DISAGREEMENT
	<104	36.0	5.1	5	14.4	2.3	5	II	II	✓
	<104	34.3	7.5	5	13.6	0.8	5	II	I	DISAGREEMENT
KIO ₄	<300	5.9	0.3	4	6.1	0.4	5	NC	I	
KMnO ₄	<300	13.9	0.7	5	6.2	0.2	5	II	I	DISAGREEMENT
	<300	14.0	0.7	5	6.5	0.5	5	II	I	DISAGREEMENT
	Bottle	21.0	0.7	5	11.7	1.3	6	II	I	DISAGREEMENT
NaClO ₃	<300	8.3	1.4	5	5.7	0.6	5	II	I	DISAGREEMENT
	Bottle	10.8	3.7	2	5.8	0.0	1	II	I	DISAGREEMENT

SCO	Size μm	UN, SCO/Fuel								
		1:1			4:1			PG		
		av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
NaNO_3	<300	22.2	1.5	5	31.6	6.2	5	had been III (revised as II)	II	✓
	<300	23.5	3.1	5	30.4	3.3	5	had been III (revised as II)	II	✓
$\text{NaClO}_4 \cdot \text{H}_2\text{O}$	<300	23	3	5	11.6	0.4	5	II	I	DISAGREEMENT
	Bottle	51	5	4	29	3.0	4	II	II	✓
Na_2O_2	<300	1.7	0.2	3	2.1	0.9	3	I	I	✓
	Bottle	22	2	7	9	2	5	I	I	✓

μm = micrometers.

av = average burning time of set of n burning times.

sd = standard deviation of set of n burning times.

n = number of burn tests in set.

s = seconds.

Times of burning used to determine above UN Packing Group assignments:

PG I: Less than or equal to 14 seconds [for KBrO_3 / Cellulose at 3:2 with bromate being 150 - 300 μm].

PG II: Greater than 14 seconds but less than or equal to 53 seconds [for KBrO_3 / Cellulose at 2:3 with bromate being 150 - 300 μm].

PG III: Greater than 53 seconds but less than or equal to 88 seconds [for KBrO_3 / Cellulose at 3:7 with bromate being 150 - 300 μm].

Not in 5.1: Greater than 100 s.

If the PG inferences from test results with 1:1 and 4:1 data differ, then the PG assignment is to the lower PG value of those inferred from the 1:1 and 4:1 test results.

Packing group classifications, based on the US test procedure and PRL experimental data using KBrO_3 , KClO_4 , and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ standards of 300- μm -or-less particle size, are listed in table 6 below. Classifications using the US bromate, perchlorate, and persulfate reference standards with the particle size being less than 300 μm yielded only 3 out of 14 classifications (**21 %**) as being the same as the published US ones. Most of the "DISAGREEMENT" cases were associated with the long combustion times for the potassium bromate and potassium perchlorate / basswood reference standards. Both SCOs had a particle size less than 300 μm . Ammonium persulfate, as a reference standard, leaves a lot to be desired. For ammonium persulfate - sawdust 1:1 mixtures, if the power is turned off too soon following the onset of smoking, the reaction rapidly ceases. Smoking commences in about 3 to 7 seconds. Seldom is open flaming observed. If the power is turned off about 25 seconds after it is initially applied, the smoking often ceases in about 90 seconds. If the power is turned off after 120 seconds, the smoking usually ceases about 200 to 250 seconds after the first application of heat. The stoichiometric oxidizer to fuel mass ratio for the ammonium persulfate-cellulose reaction is 6.3. The 1:1 mixture of ammonium persulfate-sawdust is obviously very fuel rich.

Table 6.--US SCO packing group assignments determined from NIOSH PRL experimental data using KBrO_3 , KClO_4 , and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ standards of 300- μm -or-less particle size

SCO	Size μm	US, SCO/Sawdust						
		1:1	4:1	Packing Group				
		av, s $\pm$ sd, s; n	av, s $\pm$ sd, s; n	As published in CFR	Input from 1:1 test results	Input from 4:1 test results	Assigned by using CFR definition	Agreement with CFR values (✓)
NH_4NO_3	<300	NA	NA	III				
NH_4ClO_4	<300	NA	NA	II				
$(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Reference Standard)	M&P	86 ± 1.7 , n = 3	51 ± 6.2 , n = 3	III	III	III	III	✓
"	<300	NA	NA	III				
"	Bottle	NA	NA	III				
$\text{Ca}(\text{ClO})_2$	M&P	47.5 ± 9.2 , n = 5	7.6 ± 2.1 , n = 5	II	III	I	I	DISAGREEMENT
"	<300	NA	NA	II				
"	Bottle	44.9 ± 8.1 , n = 5	15.1 ± 5.4 , n = 5	II	III	I	I	DISAGREEMENT
$\text{Ca}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$	<300	62.0 ± 9.0 , n = 3	>180, n = 3	NC	III	NC	III	DISAGREEMENT
"	Bottle	NA	NA	NC				
$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	<300	22.0 ± 3.0 , n = 3	11.3 ± 1.2 , n = 3	NC in CFR but II in (revised) UN	I	I	I	DISAGREEMENT
$\text{Mg}(\text{ClO}_4)_2$	M&P	7.7 ± 1.0 , n = 5	8.1 ± 4.3 , n = 5	II	I	I	I	DISAGREEMENT

US, SCO/Sawdust								
SCO	Size	1:1	4:1	Packing Group				
	µm	av, s ± sd, s; n	av, s ± sd, s; n	As published in CFR	Input from 1:1 test results	Input from 4:1 test results	Assigned by using CFR definition	Agreement with CFR values (✓)
"	<300	30.9 ± 8.0, n = 3 (Dried for many months at 65°C in a convection oven)		II	I	I		
KBrO ₃ (Reference Standard)	<300	34.9 ± 10.0, n = 11	10.1 ± 3.4, n = 8	II	I	I	I	DISAGREEMENT
"	Bottle	NA	NA	II				
KClO ₃	<300	14.0 ± 0, n = 1	NA	II	I			
KNO ₃	M&P	24.2 ± 5.2, n = 5	23.0 ± 3.3, n = 5	III	I	I	I	DISAGREEMENT
"	<300	NA	NA	III				
KNO ₂	<300	NA	NA	II				
"	Bottle	18.4 ± 3.5, n = 6	8.2 ± 1.8, n	II	I	I		
KClO ₄	M&P, <104	36 ± 1.0, n = 3	14.0 ± 0, n = 3	II	II	I	I	DISAGREEMENT
(Reference Standard)	< 300	39.0 ± 3.4, n = 6	NA	II	II			
KIO ₄	<300	5.8 ± 1.1, n = 2	7.1 ± 0.7, n = 3	NC	I	I	I	
KMnO ₄	<300	NA	NA	II				

		US, SCO/Sawdust						
	Size	1:1	4:1	Packing Group				
SCO	µm	av, s ± sd, s; n	av, s ± sd, s; n	As published in CFR	Input from 1:1 test results	Input from 4:1 test results	Assigned by using CFR definition	Agreement with CFR values (✓)
"	Bottle	17.0 ± 4.5, n = 4	6.6 ± 1.0, n = 5	II	I	I	I	DISAGREEMENT
NaClO ₃	<300	16.1 ± 0.9, n = 3	6.6 ± 1.1, n = 3	II	I	I	I	
"	Bottle	14.5 ± 3.0, n = 3	NA	II	I			
NaNO ₃	<300	19.2 ± 3.5 n = 5	NA	III	I			
NaClO ₄ ·H ₂ O	<300	NA	NA	II				
"	Bottle	17.3 ± 4.2, n = 3	12.2 ± 2.6, n = 5	II	I	I	I	DISAGREEMENT
Na ₂ O ₂	<300	1.5 ± 0, n = 1	1.4 ± 0, n = 1	I	I	I	I	✓
"	Bottle	14.5 ± 3.0, n = 3	7.7 ± 1.9, n = 4	I	I	I	I	✓

µm = micrometers.

av = average burning time of set of n burning times.

sd = standard deviation of set of n burning times.

n = number of burn tests in set [statistical sample size parameter].

s = seconds.

NA = not available

Bottle = as shipped

Times of burning used to determine above US Packing Group assignments:

PG I: Less than or equal to 34.9 seconds [for KBrO₃ / basswood at 1:1].

PG II: Greater than 34.9 seconds but less than or equal to 39.0 seconds [for KClO₄ / basswood at 1:1].

PG III: Greater than 39.0 seconds but less than or equal to 86 seconds [for (NH₄)₂S₂O₈ / basswood at 1:1].

Not in 5.1: Greater than 86 s.

If the PG inferences from test results with 1:1 and 4:1 data differ, then the PG assignment is to the lower PG value of those inferred from the 1:1 and 4:1 test results. To be able to make an assignment under US procedures, data is needed from both the 1:1 and 4:1 tests.

Alternative Packing Group Classifications

Packing group classifications, based on the UN test procedure, but using 150- μm -or-less KBrO_3 particles as the reference SCO, are listed in table 7. When the size range of 0 to 150 μm was used for the potassium bromate in the 3:2 mass ratio, a mean burning time one second greater than the UN published example value was achieved. Although good agreements with the burning times for the 3:7 and 2:3 mass ratios for the 0 to 150 μm particle size range of KBrO_3 were not achieved, 27 out of 38 classifications (71 %) determined were the same as the published UN classifications (PR 1).

Table 7.--UN SCO packing group assignments determined from NIOSH PRL experimental data using 150- μ m-or-less KBrO₃ particles

SCO	Size μ m	UN, SCO/Fuel								
		1:1			4:1			PG		
		av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
NH ₄ NO ₃	M&P	75	5	5	166	16	5	III	Not in 5.1	DISAGREEMENT
NH ₄ ClO ₄	<300	38	8	5	16.7	2.3	5	II	II	✓
	<300	46	4	6	15.7	2.0	5	II	II	✓
(NH ₄) ₂ S ₂ O ₈	M&P	NA			NA			III		
	Bottle	NA			>180	--	2	III		
Ca(ClO) ₂	M&P	82	11	5	8.7	0.8	5	II	II	✓
	<300	Suspect			6.0	0.7	5	II		
	<300	Suspect			5.7	1.0	5	II		
	Bottle	60	6	5	26.8	4.5	5	II	III	DISAGREEMENT
Ca(NO ₃) ₂ ·4(H ₂ O)	<300	84	22	5	152	7	4	NC (revised as Not in 5.1)	Not in 5.1	✓
	<300	73	8	3	152	11	2	NC (revised as Not in 5.1)	Not in 5.1	✓
	Bottle	138	14	2	136	14	3	NC (revised as Not in 5.1)	Not in 5.1	✓

UN, SCO/Fuel										
SCO	Size	1:1			4:1			PG		
	µm	av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
(NH ₄) ₂ Ce(NO ₃) ₆	<300	25	5	5	7.4	0.6	5	NC (revised as II)	II	✓
	<300	25	4	5	8.1	0.7	5	NC (revised as II)	II	✓
Mg(ClO ₄) ₂	M&P	15.3	1.8	5	7.4	1.5	5	II	II	✓
	<300	11.9	1.4	4	8.7	0.7	5	II	II	✓
	<300	11.3	1.4	5	10.6	0.8	5	II	II	✓
	Bottle	44.2	17.3	5	12.1	5.3	4	II	II	✓
	Bottle	21.6	6.7	5	8.6	1.3	5	II	II	✓
KBrO ₃	M&P	22.0	2.1	5	NA			II		
	<150	8.7	2.3	5	4.1	0.5	5	II	I	DISAGREEMENT
	>150 and <300	22	2.1	5	6.7	0.9	5	II	II	✓
	<300	NA			NA			II		
KClO ₃	M&P	7.9	0.7	5	4.0	0.7	4	II	I	DISAGREEMENT
	<300	NA			5.7	0.3	3	II		
	Bottle	8.1	0.4	5	5.8	0.7	5	II	II	✓
KNO ₃	M&P	22	3	5	21	2	5	III	III	✓

UN, SCO/Fuel										
SCO	Size	1:1			4:1			PG		
	µm	av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
	M&P	26	2	5	13	0.0	5	III	II	DISAGREEMENT
	<300	12	1.0	5	10	0.0	5	III	II	DISAGREEMENT
	<300	12	1.0	5	10	1.0	5	III	II	DISAGREEMENT
KNO ₂	<300	NA			NA			II		
	Bottle	35	2	5	12.7	1.1	5	II	II	✓
KClO ₄	M&P	43	7	5	12.1	1.3	5	II	II	✓
	<104	36.0	5.1	5	14.4	2.3	5	II	II	✓
	<104	34.3	7.5	5	13.6	0.8	5	II	II	✓
KIO ₄	<300	5.9	0.3	4	6.1	0.4	5	NC	II	
KMnO ₄	<300	13.9	0.7	5	6.2	0.2	5	II	II	✓
	<300	14.0	0.7	5	6.5	0.5	5	II	II	✓
	Bottle	21.0	0.7	5	11.7	1.3	6	II	II	✓
NaClO ₃	<300	8.3	1.4	5	5.7	0.6	5	II	II	✓
	Bottle	10.8	3.7	2	5.8	0.0	1	II	II	✓
NaNO ₃	<300	22.2	1.5	5	31.6	6.2	5	III (revised as II)	III	DISAGREEMENT

		UN, SCO/Fuel								
	Size	1:1			4:1			PG		
SCO	µm	av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
	<300	23.5	3.1	5	30.4	3.3	5	III (revised as II)	III	DISAGREEMENT
NaClO ₄ ·H ₂ O	<300	23	3	5	11.6	0.4	5	II	II	✓
	Bottle	51	5	4	29	3.0	4	II	III	DISAGREEMENT
Na ₂ O ₂	<300	1.7	0.2	3	2.1	0.9	3	I	I	✓
	Bottle	22	2	7	9	2	5	I	II	DISAGREEMENT

µm = micrometers.

av = average burning time of set of n burning times.

sd = standard deviation of set of n burning times.

n = number of burn tests in set.

s = seconds.

Times of burning used to determine above UN Packing Group assignments:

PG I: Less than or equal to 5 seconds [for KBrO₃ / Cellulose at 3:2 with the bromate being < 150 µm].

PG II: Greater than 5 seconds but less than or equal to 19 seconds [for KBrO₃ / Cellulose at 2:3 with the bromate being < 150 µm].

PG III: Greater than 19 seconds but less than or equal to 55 seconds [for KBrO₃ / Cellulose at 3:7 with the bromate being < 150 µm].

Not in 5.1: Greater than 55 s.

If the PG inferences from test results with 1:1 and 4:1 data differ, then the PG assignment is to the lower PG value of those inferred from the 1:1 and 4:1 test results.

Alternative Reference SCOs for Classifications

When materials are classified, to offset the effects caused by changes in laboratory conditions, procedures, or operating personnel, repetition of tests with reference chemicals is warranted. If a reference chemical or its products of combustion are carcinogenic or very toxic, it is better to replace this chemical with a less hazardous chemical — especially if the reaction is rapid or powerful. Rapid reactions are more prone to cause the products of combustion to be blown from the hood into the laboratory volume, from our experience, for hoods of volume, 0.8 m³ or less. As mentioned earlier, the very nature of these tests is such that solid debris is deposited on the interior surfaces of the hood.

A special effort was devoted toward the evaluation of KClO₃ as an alternative to KBrO₃. KClO₃ has similar reaction kinetics to KBrO₃, but does not possess the carcinogenic nature of KBrO₃. Tests were conducted with mixtures of KClO₃ and cellulose in a range of mass ratios from 1:9 to 1:0 (pure KClO₃). Experiments were also performed with KClO₃ in different particle size ranges and different total masses of mixture. Reference mass ratios of KClO₃ to cellulose were determined that produced burning times similar to the reference times published by the UN for KBrO₃. Table 8 below lists the UN Packing Groups of tested SCOs as determined by KClO₃. The tests performed using KClO₃ as a proposed reference SCO with a particle size range of 0 µm to 300 µm and mass ratios of 1:7, 1:5, and 2:1 yielded 29 out of 38 classifications (76 %) as being the same as the published UN ones. Six of the "DISAGREEMENT" cases were associated with nitrate samples; one "DISAGREEMENT" case was associated with the sodium peroxide sample being coarse; two of the "DISAGREEMENT" cases were associated with the KClO₃ and KBrO₃ samples being very fine.

Examination of the experimental data presented in Appendix E in Figure E-27 for KClO₃-cellulose with the SCO particle size being less than 0.3 mm indicates that to achieve the 100-second, 54-second, and 4-second demarcation times for the packing groups that oxidant to fuel ratios of 1.3:10, 1.7:10, and 2.53:1, respectively, be used. These values could be refined through further experimentation.

Table 8.--UN SCO packing group assignments determined from NIOSH PRL experimental data using 300- μ m-or-less KClO_3 particles

SCO	Size μ m	UN, SCO/Fuel								
		1:1			4:1			PG		
		av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
NH_4NO_3	M&P	75	5	5	166	16	5	III	III	✓
NH_4ClO_4	<300	38	8	5	16.7	2.3	5	II	II	✓
	<300	46	4	6	15.7	2.0	5	II	II	✓
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	M&P	NA			NA			III		
	Bottle	NA			>180	--	2	III		
$\text{Ca}(\text{ClO})_2$	M&P	82	11	5	8.7	0.8	5	II	II	✓
	<300	Suspect			6.0	0.7	5	II		
	<300	Suspect			5.7	1.0	5	II		
	Bottle	60	6	5	26.8	4.5	5	II	II	✓
$\text{Ca}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$	<300	84	22	5	152	7	4	had been NC (revised as Not in 5.1)	III	DISAGREEMENT
	<300	73	8	3	152	11	2	had been NC (revised as Not in 5.1)	III	DISAGREEMENT
	Bottle	138	14	2	136	14	3	had been NC (revised as Not in 5.1)	Not in 5.1	✓

		UN, SCO/Fuel								
	Size	1:1			4:1			PG		
SCO	µm	av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
(NH ₄) ₂ Ce(NO ₃) ₆	<300	25	5	5	7.4	0.6	5	had been NC (revised as II)	II	✓
	<300	25	4	5	8.1	0.7	5	had been NC (revised as II)	II	✓
Mg(ClO ₄) ₂	M&P	15.3	1.8	5	7.4	1.5	5	II	II	✓
	<300	11.9	1.4	4	8.7	0.7	5	II	II	✓
	<300	11.3	1.4	5	10.6	0.8	5	II	II	✓
	Bottle	44.2	17.3	5	12.1	5.3	4	II	II	✓
	Bottle	21.6	6.7	5	8.6	1.3	5	II	II	✓
KBrO ₃	M&P	22.0	2.1	5	NA			II		
	<150	8.7	2.3	5	4.1	0.5	5	II	I	DISAGREEMENT
	>150 and <300	22	2.1	5	6.7	0.9	5	II	II	✓
	<300	NA			NA			II		
KClO ₃	M&P	7.9	0.7	5	4.0	0.7	4	II	I	DISAGREEMENT
	<300	NA			5.7	0.3	3	II		
	Bottle	8.1	0.4	5	5.8	0.7	5	II	II	✓
KNO ₃	M&P	22	3	5	21	2	5	III	II	DISAGREEMENT

		UN, SCO/Fuel								
	Size	1:1			4:1			PG		
SCO	µm	av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
	M&P	26	2	5	13	0.0	5	III	II	DISAGREEMENT
	<300	12	1.0	5	10	0.0	5	III	II	DISAGREEMENT
	<300	12	1.0	5	10	1.0	5	III	II	DISAGREEMENT
KNO ₂	<300	NA			NA			II		
	Bottle	35	2	5	12.7	1.1	5	II	II	✓
KClO ₄	M&P	43	7	5	12.1	1.3	5	II	II	✓
	<104	36.0	5.1	5	14.4	2.3	5	II	II	✓
	<104	34.3	7.5	5	13.6	0.8	5	II	II	✓
KIO ₄	<300	5.9	0.3	4	6.1	0.4	5	NC	II	
KMnO ₄	<300	13.9	0.7	5	6.2	0.2	5	II	II	✓
	<300	14.0	0.7	5	6.5	0.5	5	II	II	✓
	Bottle	21.0	0.7	5	11.7	1.3	6	II	II	✓
NaClO ₃	<300	8.3	1.4	5	5.7	0.6	5	II	II	✓
	Bottle	10.8	3.7	2	5.8	0.0	1	II	II	✓
NaNO ₃	<300	22.2	1.5	5	31.6	6.2	5	had been III (revised as II)	II	✓

		UN, SCO/Fuel								
	Size	1:1			4:1			PG		
SCO	µm	av, s	sd, s	n	av, s	sd, s	n	As published by UN	Assigned by using UN definition	Agreement with UN published values (✓)
	<300	23.5	3.1	5	30.4	3.3	5	had been III (revised as II)	II	✓
NaClO ₄ ·H ₂ O	<300	23	3	5	11.6	0.4	5	II	II	✓
	Bottle	51	5	4	29	3.0	4	II	II	✓
Na ₂ O ₂	<300	1.7	0.2	3	2.1	0.9	3	I	I	✓
	Bottle	22	2	7	9	2	5	I	II	DISAGREEMENT

µm = micrometers.

av = average burning time of set of n burning times.

sd = standard deviation of set of n burning times.

n = number of burn tests in set.

s = seconds.

Times of burning used to determine above UN Packing Group assignments:

PG I: (2:1 KClO₃/Cellulose) Less than or equal to 4.4 s.

PG II: (1:5 KClO₃/Cellulose) Greater than 4.4 seconds but less than or equal to 43 seconds.

PG III: (1:7 KClO₃/Cellulose) Greater than 43 seconds but less than or equal to 123 seconds.

Not in 5.1: Greater than 123 seconds.

If the PG inferences from test results with 1:1 and 4:1 data differ, then the PG assignment is to the lower PG value of those inferred from the 1:1 and 4:1 test results.

The oxidizer, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as a standard, leaves a lot to be desired. If the power is turned off too soon upon the onset of smoking, the reaction between the ammonium persulfate and sawdust in a 1:1 mass ratio rapidly ceases. If the power is kept on for about 25 seconds following the initial application of heat to the pile, smoking often ceases in about 90 seconds. If the power is kept on for about 120 seconds, smoking often ceases in about 200 to 250 seconds. In a small number of instances, open flaming is involved. If the power is kept on in the fuel rich environment, the pile will continue to burn for more than ten minutes. The combustion process gives off sulfur dioxide, which for some laboratory and environmental situations can be recirculated into the work area if a scrubber system is not used on the exhaust hood.

The oxidizer, KClO_3 , with the choice of an appropriate oxidizer to fuel ratio could also serve as a suitable replacement for KBrO_3 in the US test procedure. Sufficient data exists to allow the potassium chlorate to cellulose ratios to be selected to give appropriate demarcation times for the US Packing Groups.

Exploratory tests were conducted with potassium chlorate and basswood sawdust mixtures with the oxidizer particle size range being less than 0.3 mm. The data for the chlorate-sawdust mixture with the chlorate particle size being less than 0.3 mm is also presented graphically in Figure E-6. For the smallest mass ratio, 1:6.5 (corresponding to the longest burning time), the burn time data value is a mean based on three burn tests. The other three data points corresponding to ratios of 1:1, 2.53:1, and 5:1 were single measurements. Examination of the chlorate-sawdust curve based on SCO fineness of less than 0.3 mm indicates that (1) the minimum burn time possible with the chlorate is 11 seconds at about a 2.53:1 mass ratio; (2) a burn time of 50 seconds could be obtained with about a 3:10 mass ratio; (3) and a burn time of 80 seconds could be obtained with about a 2.2:10 mass ratio. If one wanted to achieve a minimum burn time for chlorate-sawdust significantly lower than 11 seconds - say somewhere near 5 seconds - it could be achieved using chlorate of a finer size cut - say less than 150 μm as suggested in studies on burn times for the KBrO_3 -cellulose for the size cut of SCO being less than 150 μm . Inspection

of the two plots in Figure E-28 gives for the 1:1 ratio a burn time for the basswood of 14 seconds and for cellulose about 5 seconds, the latter value being about 35 % of that for the basswood. Figure E-28 also gives for the 4:1 ratio a burn time for the basswood of about 13 seconds and for cellulose about 5 seconds, the latter value being about 40 % of that for basswood.

In conducting the US tests, according to the prescribed procedure, the power applied to the heating wire was turned off shortly after the onset of open flaming. To evaluate the effect of leaving the heating wire turned on until the cessation of open flaming, one test (# 733) of potassium chlorate-sawdust at a 1:6.5 mass ratio with the chlorate being less than 0.3 mm in particle size was conducted. This gave a burn time of 91 seconds which is significantly less than the 156-second mean burn time for the three tests (# 734, 735, and 736) conducted with the heating power cut off just after the onset of open flaming.

Table 9 provides US SCO Packing Group assignments as determined by burning times of 300- μm -or-less KClO_3 particles. Classifications using a set of reference standards based on 300- μm potassium chlorate mixed with basswood yielded only 7 out of 14 classifications (50 %) as being the same as the published US ones.

Table 9.--US SCO packing group assignments determined by burning times of
300- μ m-or-less KClO_3 particles

SCO	Size μm	US, SCO/Sawdust						
		1:1	4:1	Packing Group				
		av, s $\pm$ sd, s; n	av, s $\pm$ sd, s; n	As published in CFR	Input from 1:1 test results	Input from 4:1 test results	Assigned by using CFR definition	Agreement with CFR values ($\checkmark$)
NH_4NO_3	<300	NA	NA	III				
NH_4ClO_4	<300	NA	NA	II				
$(\text{NH}_4)_2\text{S}_2\text{O}_8$ (Reference Standard)	M&P	86 ± 1.7 , n = 3	51 ± 6.2 , n = 3	III	III	III	III	$\checkmark$
"	<300	NA	NA	III				
"	Bottle	NA	NA	III				
$\text{Ca}(\text{ClO})_2$	M&P	47.5 ± 9.2 , n = 5	7.6 ± 2.1 , n = 5	II	II	I	I	DISAGREEMENT
"	<300	NA	NA	II				
"	Bottle	44.9 ± 8.1 , n = 5	15.1 ± 5.4 , n = 5	II	II	II	II	$\checkmark$
$\text{Ca}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$	<300	62.0 ± 9.0 , n = 3	>180, n = 3	NC	III	NC	III	
"	Bottle	NA	NA	NC				
$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	<300	22.0 ± 3.0 , n = 3	11.3 ± 1.2 , n = 3	NC in CFR but II in UN	II	II	II	$\checkmark$ with UN
$\text{Mg}(\text{ClO}_4)_2$	M&P	7.7 ± 1.0 , n = 5	8.1 ± 4.3 , n = 5	II	I	I	I	DISAGREEMENT

US, SCO/Sawdust								
SCO	Size	1:1	4:1	Packing Group				
	µm	av, s ± sd, s; n	av, s ± sd, s; n	As published in CFR	Input from 1:1 test results	Input from 4:1 test results	Assigned by using CFR definition	Agreement with CFR values (✓)
"	<300	30.9 ± 8.0, n = 3 (Dried for many months at 65°C in a convection oven)		II	II			
KBrO ₃ (Reference Standard)	<300	34.9 ± 10.0, n = 11	10.1 ± 3.4, n = 8	II	II	I	I	DISAGREEMENT
"	Bottle	NA	NA	II				
KClO ₃	<300	14.0 ± 0, n = 1	NA	II	II			
KNO ₃	M&P	24.2 ± 5.2, n = 5	23.0 ± 3.3, n = 5	III	II	II	II	DISAGREEMENT
"	<300	NA	NA	III				
KNO ₂	<300	NA	NA	II				
"	Bottle	18.4 ± 3.5, n = 6	8.2 ± 1.8, n	II	II	I	I	DISAGREEMENT
KClO ₄	M&P, <104	36 ± 1.0, n = 3	14.0 ± 0, n = 3	II	II	II	II	✓
	< 300	39.0 ± 3.4, n = 6	NA	II	II			
KIO ₄	<300	5.8 ± 1.1, n = 2	7.1 ± 0.7, n = 3	NC	I	I	I	
KMnO ₄	<300	NA	NA	II				

		US, SCO/Sawdust						
	Size	1:1	4:1	Packing Group				
SCO	µm	av, s ± sd, s; n	av, s ± sd, s; n	As published in CFR	Input from 1:1 test results	Input from 4:1 test results	Assigned by using CFR definition	Agreement with CFR values (✓)
"	Bottle	17.0 ± 4.5, n = 4	6.6 ± 1.0, n = 5	II	II	I	I	DISAGREEMENT
NaClO ₃	<300	16.1 ± 0.9, n = 3	6.6 ± 1.1, n = 3	II	II	I	I	DISAGREEMENT
"	Bottle	14.5 ± 3.0, n = 3	NA	II	II			
NaNO ₃	<300	19.2 ± 3.5 n = 5	NA	III	II			
NaClO ₄ ·H ₂ O	<300	NA	NA	II				
"	Bottle	17.3 ± 4.2, n = 3	12.2 ± 2.6, n = 5	II	II	II	II	✓
Na ₂ O ₂	<300	1.5 ± 0, n = 1	1.4 ± 0, n = 1	I	I	I	I	✓
"	Bottle	14.5 ± 3.0, n = 3	7.7 ± 1.9, n = 4	I	II	I	I	✓

µm = micrometers.

av = average burning time of set of n burning times.

sd = standard deviation of set of n burning times.

n = number of burn tests in set [statistical sample size parameter].

s = seconds.

N. 5.1 = not in Division 5.1.

NA = not available

Bottle = as shipped

Times of burning used to determine above US Packing Group assignments:

PG I: Less than or equal to 11 seconds [for KClO₃ / basswood at 2.53:1].

PG II: Greater than 11 seconds but less than or equal to 50 seconds [for KClO₃ / basswood at 3:10].

PG III: Greater than 50 seconds but less than or equal to 80 seconds [for KClO₃ / basswood at 2:10].

Not in Division 5.1: Greater than 80 seconds.

If the PG inferences from test results with 1:1 and 4:1 data differ, then the PG assignment is to the lower PG value of those inferred from the 1:1 and 4:1 test results. To be able to make an assignment under US procedures, data is needed from both the 1:1 and 4:1 tests.

Experimental Considerations

COMPARISON AND CONTRAST OF THE US AND UN PROCEDURES :

The advantages and disadvantages associated with the US and UN test protocols are tabulated in tables 10 and 11 below, respectively.

The analysis of the information presented in these two tables provides a strong basis for recommending that the US adopt a "refined" version of the UN test protocol. The refined version would include replacing the three potassium bromate / cellulose mass ratios used as standards with three potassium chlorate ones. If it were decided that in the "interim" or "transitional" time period for adopting the UN test protocol to pursue the US test protocol, then some key changes should be made; these include replacing the current set of three U.S. reference standards (potassium bromate, potassium perchlorate, and ammonium persulfate) with potassium chlorate at three different oxidizer-fuel mass ratios, and increasing the sample size number to five. If one were to replace the sawdust with cellulose of the fineness used in the UN test protocol, there would be only minor differences between the refined US and UN test protocols.

We turn now to a discussion in greater detail of the above and other related items relevant to a comparison and contrast of the two protocols. The US test procedure has advantages over the UN procedure in cost per test set and in accurately determining the length of the combustion period for the less reactive oxidizers. Admittedly, burning three samples of a material is less costly than burning five samples. Sometimes, but not always, burning three samples provides a basis for rejection of an outlier value for the burning time.

Table 10.-- Advantages and disadvantages associated with the US SCO test protocol

Item	Advantage	Disadvantage	Comments
Number of replications	1. The sample size number reduces cost.	1. The small sample size number makes it difficult to deal with outliers and leads to an inappropriately large estimate of the parent population's standard deviation in the mean burn time.	The three test sample size should be increased from three to five.
Standard deviation		1. The usually large magnitude of the standard deviation along with the small sample size are not very supportive of hypothesis testing for comparison of means.	By replacing the sawdust by the cellulose specified in the UN test protocol, one can expect lower standard deviations.
Geometric shape of heater wire	1. The "open" circle is easy to construct.		This may not be significant.
Setting the heating wire current to achieve a specified temperature	1. It focuses attention on the temperature of wire, which is of physical importance for chemical kinetic processes are temperature dependent.	1. It is indirectly addressed by specifying "bare" wire temperature of 1,000 °C.	One needs to have a calibration chart to set test current based on optical pyrometry.
Choice of fuel		1. The sawdust choice allows too much variation in composition. 2. It is difficult to acquire same fuel for replenishment, thereby adding an unnecessary complication to the measurement process for the mean burn time and its standard deviation.	The sawdust should be replaced by the cellulose specified in the UN SCO test protocol.
Particle size cuts	1. Materials are easy to sieve	1. Often there is a mismatch between the particle size of the SCO and the fuel which results in segregation of the "mixed" oxidizer and fuel upon formation of the test pile, leading to an increase in the standard deviation of the mean burn time. 2. Specifying no lower boundaries for the size cuts, could allow very reactive mixtures of KBrO_3 and sawdust to be created by some experimentalists.	More thought should be given to the particle size distribution for the oxidizers.

Reference standards	1. There is simplicity with the 1:1 approach; 2. The specification of the reference SCO being less than 300 μm is in the right direction for obtaining demarcation times between PGs II and III and between III and "not in 5.1"	1. The choice of reference standards includes a human carcinogen (potassium bromate) and a sulfur dioxide generator of long duration. The oxidizer, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as a standard, leaves a lot to be desired. If the power is turned off too soon upon the onset of smoking, the reaction between the ammonium persulfate and sawdust in a 1:1 mass ratio rapidly ceases. If the power is kept on for about 25 seconds following the initial application of heat to the pile, smoking often ceases in about 90 seconds. If the power is kept on for about 120 seconds, smoking often ceases in about 200 to 250 seconds. In a small number of instances, open flaming is involved. 2. The coarseness of 300 μm for the SCO in 1:1 formulation involving sawdust of particle size $< 1,600 \mu\text{m}$ makes (one) it difficult to achieve a small demarcation time (on the order of 5 - 10 seconds) between PGs I and II, thereby resulting in a "poor" performance record in classifying SCOs (two) the time window for the PG II to III is too compressed, thereby resulting in a "poor" performance record in classifying SCOs. 3. The 1:1 approach impedes selection of an alternative reference SCO or set of SCOs that gives adequate demarcation times commensurate with obtaining a good classification performance record.	The set of reference SCOs should be replaced by potassium chlorate of sufficient fineness with three appropriate oxidizer/fuel mass ratios to give 5- to 10-second, 50-second, and 80- to 100-second demarcation times.
Definition of burn time	1. Does not include the induction period (prior to the onset of smoking or open flaming) for energetic to moderately reactive SCOs.	1. For the less reactive SCOs in PG II and III, which are in some instances characterized by a small period of open flaming, the estimation of burn time can be "artificially" low and therefore misleading. 2. For the more energetic (rapid reacting) SCOs as those in PG I or in PGII but close to the demarcation time for PG I and II, it is hard to accurately determine the burn time without recourse to video records.	

Duration of application of power to the heating wire (power turned off just after the onset of combustion)	1. For the least reactive SCOs a more realistic estimate of the actual burn time is achieved because the measuring time is based on heat input from the reaction and not from the heater wire prolonging the reaction. 2. Prolongs the life of the heater wire - which is not all that important as long as a wire does not break during the application of heating in a test.	1. Turning the power off during the test adds complexity to the operation for the more energetic reactions - one has to act rapidly to shut the power off following the onset of combustion. Otherwise it artificially increases the standard deviation in the measurement of the burn time. 2. If the heating power is turned off prematurely, the reaction may not have achieved a temperature to adequately get the reaction underway, thereby giving misleading information.	Although the tradeoffs indicate that it is better to keep the heating on and include the induction period as part of the burn time, for slow reactions one cannot differentiate between the glowing of the wire and the glowing of the pile.

Table 11.-- Advantages and disadvantages associated with the UN SCO test protocol

Item	Advantage	Disadvantage	Comments
Number of replications	1. The large sample size number of five makes it easier to identify outliers and provides a better statistical basis for their rejection. 2. The large sample size makes the estimation of the parent population standard deviation of the mean burn time more realistic than that associated with a sample size of three, taking into account the possibility of rejection of one of the three measurements as an outlier.	1. The large sample size number increases the amount of time to conduct the test and the associated cost - which may or may not be all that significant when one focuses on the quality of information desired and the test charges.	A statistical criteria should be specified as a guideline for rejection of an outlier. Rather than restrict the sample size to five, the preferred wording should be at least five. The bigger the sample size, the better the basis would be for rendering a statistical comparison of either means or standard deviations. The greater the statistical complexity, the greater the cost for conducting the tests.
Standard deviation	1. The usually small magnitude of the standard deviation along with the large sample size are supportive of hypothesis testing for comparison of means.		This is a most important point.
Geometric shape of heater wire	1. The "open-indented" circle provides greater contact area for heat transfer during heating than the "open" one for the US test protocol.	1. Requires more effort to construct - which may or may not be all that significant.	
Setting the heating wire current to achieve a set power input for ignition	1. Specifying a power level of 150 watts simplifies matters.		For 30-cm length of AWG 18 Nichrome wire, 150 watts input corresponds closely to a "bare" wire temperature of 1,000 °C as measured by optical pyrometry

Choice of fuel	1. The choice of cellulose reduces variation in composition, thereby better controlling the mean and its associated standard deviation. 2. It is relatively easy to acquire same fuel for replenishment, thereby avoiding an unnecessary complication to the measurement of the mean burn time and its standard deviation.		The choice of cellulose as the fuel is a better choice than softwood sawdust.
Particle size cut for fuel	1. With the fine cellulose there is less of a mismatch between the particle size of the SCO of less than 300 μm in particle size, thereby avoiding the segregation of the "mixed" oxidizer and fuel upon formation of the test pile, leading to a smaller standard deviation of the mean burn time than with sawdust of size $< 1,600 \mu\text{m}$.	The fineness of the cellulose gives a mismatch with some of the coarser (but less reactive) SCOs leading to segregation when the conical shaped pile is formed.	The tradeoff in using the small sized cellulose is acceptable, considering the emphasis on characterizing with greater accuracy the more reactive SCOs.
Reference standards	1. The coarseness of 150 to 300 μm for the SCO in the 3:2 formulation involving fine cellulose makes it difficult to achieve a small demarcation time (on the order of 4-5 seconds between PGs I and II, thereby resulting in a "poor" performance record in classifying SCOs. 2. The 150-300 μm particle size cut approach for reference SCOs impedes selection of an alternative reference SCO or set of SCOs that gives adequate demarcation times commensurate with obtaining a good classification performance record.		Preliminary studies with potassium chlorate of a size cut of 0 to 150 μm as a suitable replacement for the human carcinogen has suggested that an appropriate set of mass ratios can be selected to give demarcation times between packing groups that will result in good classification agreement with UN published packing group assignments.

Definition of burn time	1. Includes induction period (prior to the onset of smoking or open flaming) for moderate to less reactive SCOs, thereby avoiding the estimation of an "artificially" low burn time associated with a test in which there is a long induction time and a relatively short duration of open flaming. 2. For the more energetic (rapid reacting) SCOs as those in PG I or in PGII but close to the demarcation time for PG I and II, it simplifies the determination of the burn time because it avoids having to subtract off the induction period.		
Duration of application of power to the heating wire (power kept on and not turned off after the onset of combustion)	1. Keeping the power on adds simplicity to the operation for studying the more energetic reactions - one does not have to act rapidly to shut the power off following the onset of combustion, thereby avoiding an unnecessary increase in the estimated parent standard deviation of the the mean burn time. 2. Because the heating power is not turned off prematurely, the reaction is sustained.	1. Shortens the life of the heater wire - which may not be all that important as long as a "new" wire does not break during the application of heat in a test. 2. For the least reactive SCOs such as ammonium persulfate, the rate of application of heat dominates over that from the rate that heat is released from the combustion, thereby not making a true measurement of the burn time.	The tradeoffs indicate that it may be better to keep the heating on and include the induction period as part of the burn time. To what extent ignition of the pile from a wire placed near the top would impact on matters still merits investigation

How to compare means and handle outliers (also called stragglers or extreme values) in classification work needs to be addressed. If an outlier is rejected from a set of three measurements, there could be a problem in gaining acceptance of the decision. Using a sample size of two to estimate the standard deviation in the mean burning time does not make much sense. With two measurements, one is better off referring to the spread or range of values. The expected larger standard deviation associated with a three-sample test set, as opposed to that with a five-sample test set, would make hypothesis testing of means less confident. It is better to spend an additional hour or two of laboratory effort to conduct several more tests (at least five in total) to reduce experimental uncertainty and provide an improved basis for the rejection of an outlier should such occur than to simplify the work load and reduce the cost by doing the minimum effort. Considering the range of magnitudes of the standard deviations in SCO tests and the ease and cheapness with which the tests can be conducted, one might effectively argue that a sample size of 10 should have been used rather than the five called for by the current UN procedure.

Consideration should be given to evaluating whether the t-test should be employed in SCO test protocol to compare mean burn time for the material being classified with the mean burn time for the appropriate reference standards. This entails (1) confirming that a correct statistical basis exists for comparing the SCO means by use of the t-distribution and (2), selecting the appropriate levels of significance (α) to use. There is a need to (1) identify a statistical criterion for rejection of an outlier that would have wide spread acceptability in the science community and (2) establish criteria to determine whether additional tests are needed and, if so, how many. Further information on how these statistical matters can be effectively addressed is presented in Appendix H.

The use of video recording equipment improved the accuracy of the burning time determination. It is of great importance for determining the burn time for the more rapid reactions. The use of the VCR record permits a review of the test and opportunity for others to witness the test and concur or disagree with the time taken as the cessation of open flaming or smoking. To help mark the onset of heating in the video record a small light bulb could be used in the field of view. A parallel current to a small light bulb

would help to mark the event when power is applied to the heater wire during a test.

The length of the burning time interval in the US procedure in some instances can be determined more accurately than in the UN procedure because the US procedure (1) excludes the time associated with heating of the mixture up to ignition which is significant in the case of the more moderately reacting oxidizers and (2) removes much of the ambiguity in determining the end of combustion for the slower burning materials because the heater wire current is turned off just after ignition occurs. However, in the case of the less reactive oxidizers a minute might go by before smoking or open flaming occurs and when the duration of the smoking or flaming is short - say four seconds, the "short" burning time recorded would in essence distort the proper characterization of the oxidizer. One could conclude that the oxidizer belongs in Packing Group I when in fact it belongs in a much higher packing group.

For the more rapid reactions with open flaming, it was relatively easy to measure the burning time. Within the UN procedure for the slower reactions, it was difficult to differentiate between the light emitted by the burning pile and the light from the incandescent wire near the end of combustion. For the slower burning SCOs, possibly a more quantitative criterion could be specified for the end of combustion such as the peak temperature in the pile as measured by a thermocouple record or by a record from a pyrometer. In spite of the ambiguity in determining the UN burning time, the standard deviations of the mean burning time for the UN tests were generally less than the standard deviations for the US tests.

If the criterion of cessation of glowing were used, as called for in the UN procedure, then many of the burning times would have exceeded three minutes. Also, glowing combustion was easily hidden by burned material forming a shell around the glowing core of the pile. This glowing core, often mistaken for the glowing wire, was observed when the current to the ignition wire was stopped after visually deciding that burning had ceased. When the ignition wire was being removed from the pile, the glowing core was observed. Several times the smoke generated by burning in the 0.8-m³ hood obscured the view of the pile enough to not make accurate determination of the end of burning possible.

One advantage of sawdust over cellulose was the marked contrast in color between sawdust and most of the SCOs. This contrast permitted an easy determination of complete mixing of the sawdust and

a SCO for some materials. However, it is better to select a mixing procedure and time that is less reliant on visual observation and mixing intensity by the operator to minimize the impact of human error and dependence upon a particular operator's ability to judge by eye when mixing is adequate.

Another disadvantage with using sawdust was that SCO particles of high density would tend to sink below the less dense and larger sawdust particles preventing complete mixing. Even if complete mixing were accomplished, the process of pouring the mixture to build a conical pile would sometimes tend to separate the components. The US procedure could be significantly improved by replacing the < 1,600 μm sawdust with cellulose of particle size similar to that used in the UN test procedure. Special consideration should be given to implementing this recommendation if a decision is made to keep the US protocol.

In the early stages of this study, tests were conducted with wood flour. It was observed that when combining the wood flour with SCOs that the mixing of the two substances was more complete than was experienced later with sawdust. The wood flour possessed a smaller mean particle size than the sawdust and generally burned more rapidly than the sawdust. Variations of the burning time with power to the ignition wire for KNO_3 and wood flour at 1:1 and 4:1 ratios are shown in Appendix I. Figures I-1 and I-2 show the pronounced effect of the heating power upon the ignition process.

Another advantage in the US test procedure was that the round shape of the US wire was relatively easy to fabricate by wrapping the wire around a cylinder of appropriate diameter to allow for the elasticity of the wire. However, this is not all that significant when time is not a critical issue.

A logistics problem was experienced with sawdust. There was some difficulty in locating a vendor of softwood sawdust in the northern part of the US. There is not only the problem of acquiring a similar kind of sawdust at a later date, but also one that has not been contaminated by other kinds of "floor" dust and waste material swept up from the floor at the saw mill or lumber yard cutting room. The cellulose used in conducting the SCO tests had a mean particle length of 125 μm . It is readily available in a "pure" and uniform state. It was purchased from Whatman Labsales, Inc. which also has offices in the UK. There are other vendors in the US for cellulose, one being the Sigma Corporation. The cellulose from the

Sigma Corporation has a mean particle size of 25 μm . This would be useful in characterizing the effect of particle size of the fuel on the burn time.

This study underscored the importance of three important parameters influencing burn time: (1) the particle size of the oxidizer, (2) the oxidizer to fuel ratio, and (3) the storing / processing / handling of the oxidizer used to prepare mixtures for testing. The first two factors may be obvious. The third factor merits some comments. If oxidizers that have an affinity for moisture are heated in a convection oven open to ambient air, then their reactivity is diminished. If oxidizers are stored in the open air, their reactivity can be neutralized. If oxidizers are stored in a desiccator chamber with "expired" desiccant, then their reactivity can be diminished. If oxidizers are heated for too long of a period of time at near or above their decomposition temperature, then their reactivity will be diminished. If oxidizers are contaminated, their reactivity can change - increase or decrease, depending upon the nature of the contaminant. If oxidizers having water of hydration are heated, they may go from a solid state into a liquid state.

LOCATION OF IGNITER WIRE AND METHOD OF FORMING THE PILE:

In some instances during the early stages of the burning, the gases generated from the heating element being placed at the bottom of the pile caused a rapid redistribution of the pile. Following the specification that the piles be ignited on the bottom caused considerably scattering about the inside of the hood of many mixtures during the initial part of the burning period. Both the US and the UN procedures require that the wire be placed at the bottom of the mixture pile. Many piles collapsed on ignition from the rush of gas and smoke from the pile or the piles would be dispersed about the inside of the exhaust hood by the product gas pressure. Much of the dispersed material would often not react -- thus reducing the value of the burning time that would have been measured if total reaction had occurred.

A stainless steel or ceramic restraining ring around the conical pile would reduce the tendency of the pile to scatter during the initial stage of combustion, thereby reducing the scatter in the data and increasing the amount of reactants participating in the combustion. A wire mesh ring about 10 cm in

diameter and about 2.5 cm high with a small opening to allow heater wire with fiber glass sleeving to pass through may be helpful in better controlling the test.

Also investigating different locations for the heater wire should be investigated. One location that ought to be considered would entail placing the heater wire higher up and possibly on top of the pile after the pile has been formed. This effort implies that the effect of varying the shape of the heater wire on burn time should also be investigated. Placing the heater wire on or nearer the top would be particularly desirable for burning peroxides. Out of nineteen tests conducted with Na_2O_2 , every test but one destroyed the ignition wire on the bottom of the pile. Other modes of ignition are possible and merit investigation.

The UN committee on hazardous goods specified in detail the shape of a laboratory container to use to form conical piles of the SCO-fuel mixtures. To accomplish this a laboratory funnel was used. Following this specification caused considerable redistribution of many mixtures when the funnel was removed from the pile. Sometimes the removal of the funnel from these compressed piles often disturbed the pile enough so that the pile would collapse, resulting in its angle being near the angle of repose. Some mixtures overflowed the funnel, making compression necessary using a tamping rod in order to fill the funnel. Compression of a mixture inside a funnel could be dangerous depending on the type of SCO, particle size, and type of contamination of the mixture. Working with confined mixtures of oxidizers and fuels requires a special safety awareness. Such a confined mixture is often unstable and when subjected to heat could explode. Working with the mixture of fuel and oxidizer is a dangerous situation with or without the funnel. Therefore, after confirming electrical continuity the heating wire power should be locked out before forming the pile. Tests were conducted using both a funnel and pouring mixtures at their angles of repose onto the ignition wire. Since little difference in the burning times between the two methods of forming piles was observed, in the interest of eliminating working with confined mixtures of oxidizers and fuels, it is recommended that the pile be formed by pouring the mixture to form a conical or dome-shaped pile over the heating wire.

SPECIFICATION OF HEATING WIRE:

Four different sizes of heater wire were tested. The sizes ranged from American Wire Gauge (AWG) 24 to AWG 18. The chemical composition of these wires was 80% nickel and 20% chromium. Table 12 below includes electrical properties of 30-cm lengths of Omega Engineering wire with the chemical composition described above, various diameters, and at 1,000° C. Calibrating the temperature of the 30-cm long pieces of Nichrome wire as a function of electrical current to fulfill its specification for the US test protocol and to characterize the surface temperature of the "bare" wire used in the UN test protocol was accomplished using an optical pyrometer. The amperes listed were interpolated from graphs of the temperature, measured by an optical pyrometer, of each size of wire in the US and UN configurations as a function of electrical current. The values of voltage were calculated from the values of resistance and the values of current. Refer to graphs J-1 through J-6 in Appendix J to obtain temperatures of wires at other values of current.

Table 12.--Electrical properties of Omega Engineering's 80% Ni and 20% Cr heating wire at 1,000° C as measured by an optical pyrometer

AWG	Diam, mm	Amperes	Volts	Watts
18	1.016	19.4	7.8	150
20	0.813	13.2	8.2	109
22	0.643	9.8	9.8	96
24	0.511	7.6	12.0	91

Because the UN wire size (0.6 mm diam) is fragile and the wire with size and electrical resistance (6 Ω /m) specified by the UN was not readily obtainable, a wire of American Wire Gauge (AWG) size 18 (1.016 mm diam) was selected as the ignition wire. (A search by an Omega Engineering representative of its European facility failed to locate a wire that met the UN specifications.) This wire was cut to an electrical-path length of 30 cm, appropriately bent, and heated by 150 W of electrical power achieved with a current of 19.4 amperes. (When this wire is heated with 150 W in open air, a temperature of about 1,000° C, is obtained which coincides with that specified in the US procedure.)

The US procedure stipulates that the heating wire should be positioned one mm above the test surface. It is difficult to maintain the one-mm elevation specification for the placement of the heater wire in the US procedure. To try to meet this specification, at least three ceramic insulator rings or sleeves were distributed evenly around the wire. Our experience with these insulators was that the heat trapped or released from spuriously reacting material within the insulators tended to often elevate the temperature of the wire above its melting point during the combustion period thus breaking the wire. In one test, when a 5-cm-long, two-hole insulator sleeve with parallel holes through its length was placed around the lead and terminal parts of the wire, the insulator broke in the middle during heating with an explosive like force. Possibly when the material that had collected within the insulator tubes reacted it caused either a rise in "local" pressure or uneven heating that set up sufficient stress to break the insulator into two pieces. The manual fabrication of the wire configuration usually leaves the wire with at least a one-mm-high wave around its path on the test surface.

The UN wire configuration required more time to construct than the US wire one. The UN configuration was accomplished by bending the wire to fit a paper template of the full-size wire form. An important point is to maintain the same wire shape from test to test.

SAFETY AND HEALTH ISSUES AND HAZARD MODEL FOR EXHAUST HOODS:

In lieu of installing a fume extraction system on the exhaust pipe from a laboratory hood used for the later part of this research effort, a vertical stack (about 8 m high) was placed on the exhaust pipe from the fan. It was felt by the PRL safety personnel that the tall stack would facilitate dilution of the exiting gas and smoke with air to below a safe concentration before any possible recycling back into the laboratory. One problem with this tall stack arrangement is that a cloud of combustion products can descend from the top of the stack and re-enter the laboratory during a windless atmospheric condition. Another possible problem with this arrangement, and even with a fume extraction system were such employed, is the considerable inertia of the column of air in the stack or in an extraction system. When rapid reactions occur, the gas in the hood is rapidly pressurized because the exiting gas stream from the top of the hood

requires significant time to accelerate to the flow rate of gas generated in the hood. The hood volume (not including the fan and stack volumes) in both laboratories used for testing was about 0.8 m³. For the 1:1 mixture of Na₂O₂ and cellulose, the average volumetric production rate at atmospheric pressure was 29 l/s (see table 13 below or K-3 in Appendix K).

Table 13.-- Rate of production of gaseous products for various SCO-cellulose reactions

Chemical Model	SCO-to-Fuel Mass Ratio ¹	Stoichio. Oxid.-to-Fuel Mass Ratio	Chemical in Excess	Burn Time, s	'Hot' ² Gas Flow Rate, L/s
$12\text{Na}_2\text{O}_2 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 7\text{Na}_2\text{O} + 6\text{CO}_2 + 10\text{NaOH}$	1	5.77	Cell.	1.7	³ 29.2
$4\text{KBrO}_3 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 4\text{KBr} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	⁴ 4	4.12	Cell.	4.1	³ 19.4
$4\text{KClO}_3 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 4\text{KCl} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	3	3.02	Cell.	5.5	³ 17.4
$4\text{NaClO}_3 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 4\text{NaCl} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	4	2.63	Oxid.	5.7	14.4
$3\text{KIO}_4 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 3\text{KI} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	4	4.26	Cell.	6.1	10.8
$6\text{Ca}(\text{ClO})_2 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 6\text{CaCl}_2 + 5\text{H}_2\text{O} + 6\text{CO}_2$	4	5.29	Cell.	5.7	10.3
$8\text{KMnO}_4 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 8\text{MnO}_2 + 8\text{KOH} + 6\text{CO}_2 + \text{H}_2\text{O}$	4	7.80	Cell.	6.2	9.5
$24(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6 + 49\text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 192\text{NH}_3 + 53\text{H}_2\text{O} + 294\text{CO}_2 + 12\text{Ce}_2\text{O}_3$	4	1.66	Oxid.	7.4	8.1
$3\text{Mg}(\text{ClO}_4)_2 + 2\text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 3\text{MgCl}_2 + 10\text{H}_2\text{O} + 12\text{CO}_2$	4	2.07	Oxid.	8.7	7.9
$3\text{KClO}_4 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 3\text{KCl} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	⁵ 4	2.56	Oxid.	12.1	6.3
$8\text{KNO}_2 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 8\text{KOH} + 4\text{N}_2 + \text{H}_2\text{O} + 6\text{CO}_2$	⁶ 4	4.20	Cell.	12.7	4.4

¹ All particle size ranges are from 0 to 0.3 mm unless indicated otherwise.

² 'Hot' means average gas flow rate at 1,800° K unless indicated otherwise.

³ Calculated adiabatic flame temperatures were used.

⁴ Particle size range was 0 to 0.15 mm.

⁵ SCO was ground in a mortar and pestle but not sieved.

⁶ SCO particles were not reduced in size.

As a result of some reactions, the local pressure in the hood exceeded the ambient pressure in the laboratory. When this happened, gas, smoke, and particulates jetted out of the hood and into the laboratory. To help prevent this jetting for the slower reactions, it was found by trial-and-error that the glass hood sash should be opened only about 2 cm and that the plane of the base of the mixture pile should be at least 10 cm above bottom of the hood sash. However, when conducting some of the potassium chlorate-cellulose reactions under low humidity conditions and with the sash raised only a few centimeters, there was such a rapid pressurization within the hood that the glass sash was pushed rather abruptly against the outer surface of its channel with a "bang."

For the very fast reactions, the height of the sash opening was selected to be high. In a few instances (Na_2O_2 being less than 300 μm), the cloud traveled horizontally 5 m. With such violent reactions and with the sash raised relatively high it is natural to expect contamination of the laboratory work area. Because of the anticipated violence of the sodium peroxide-cellulose reaction involving peroxide particles of less than 300 μm in size, to avoid breakage of the glass sash it was elevated about 20 cm above the bottom of the hood. Using a height of 20 cm resulted in the plane of the base of the reacting mass being below the bottom of the sash. With 30-gram mixtures raising the sash to a high level was simply a matter of choosing "the lesser of two evils." When conducting violent oxidizer-fuel reactions with 30-gram mixtures in a relatively small hood, either jetting is to be expected with the sash raised up high or flying glass from breakage of the hood sash when the sash is only raised a few centimeters. Therefore, when working under the aforementioned conditions, experimentalists should be in a safe location.

Although in the experimental work with sodium peroxide-cellulose mixtures made with the SCO being less than 300 μm , a safety shield was not used, the experimentalists took precautionary measures by raising the hood sash and initiating the burn test from outside the laboratory. Most likely the violent force would have shattered the hood sash had it been kept in a lowered mode, so in the course of doing the violent tests with the sash raised only a few centimeters either the sash window would have needed to be reinforced or replaced from test to test. Clearly, because of the potential violence in conducting SCO-

fuel reactions, a plastic safety shield should be employed when conducting burn tests. It should become part of the standard operating procedures for those doing classification testing. Using a safety shield would help to deflect the flying glass from the hood window should the material react with great violence.

In general, the air flow through and the pressure within the 0.8-liter hoods allowed the hood to contain the combustion reaction products. Only rarely did the local pressure from the generation of reaction products near the sash opening of the hood exceed the ambient air pressure in the laboratory. The measured air velocity through the 2-cm gap at the bottom of the glass sash was in the range from 400 m/min to 600 m/min for the hoods we used. See figures A-1 and A-2 in Appendix A. For some laboratory situations, it may be necessary to block open a door (as far from the laboratory as possible) leading into the laboratory building. To keep the combustion products in the hood farther away from the hood's air inlet, the test surface within the hood should be elevated. We positioned the test surface on fire bricks about 10 cm above the bottom of the hood. All air leaks into the hood, other than the air flowing under the bottom of the glass sash, should be plugged. (A potential location for a leak to occur is between the sash and the upper portion of the hood. A leak here might show up only under dynamic testing using a "smoke" bomb under conditions simulating the pressure rise associated with explosion flames. Normal testing procedures for an exhaust hood involving low pressure rises give deceiving results.)

To control laboratory contamination - a most important point when conducting tests with very energetic and rapidly reacting SCO - a hood with a large volume capacity and flow rate should be used because it would better absorb the reaction pressure pulses and contain the products. To control laboratory contamination from carcinogenic or extremely toxic SCOs, a wash down hood should be used. If large amounts of oxidizer are to be ground and sieved, it is better to dedicate a separate hood for this operation.

For the more reactive oxidizers, to avoid jetting of the reaction products and reactants out into the laboratory area, smaller mixture masses should be used to evaluate whether there might be a problem with 30-gram mixtures. The volume of gaseous products generated can be decreased by diminishing the total mass of mixture burned to about 20 g or less. Six tests with KClO_3 and cellulose were conducted to

determine the effect of the mass of the mixture on the burning times. It was found that less massive mixtures yielded smaller burning times for the 1:1 mass ratio. See figure E-41 in Appendix E.

Other tests conducted with KClO_3 indicated that mixtures slightly deficient in the SCO reacted the fastest. The data indicated that the minimum burning time occurred for mixtures with mass ratios between 2 and 3. The stoichiometric ratio for the KClO_3 -cellulose mixture was calculated to be 3.02. See table K-1 for stoichiometric ratios for selected reactions.

For some of the more energetic reactions based on 30 g of mixture and an adiabatic flame temperature of $1,800^\circ \text{K}$, a volumetric production rate was calculated. A summary of the production rates along with the chemical models and measured burning times for eleven reactions at $1,800^\circ \text{K}$ are listed in table 13. The reasonableness of this flame temperature was based on calculations from the NASA Lewis CEA program (PR 5, 6) with three SCOs (Na_2O_2 , KBrO_3 , and KClO_3) each reacting with cellulose and having flame temperatures of 1786°K , 2431°K , and 2435°K , respectively.

The potassium bromate reaction ejected combustion products between the top of the glass sash and the sash channel wall of first hood used. This leakage path was then plugged for subsequent tests. Potassium chlorate, sodium chlorate, and sodium peroxide reactions ejected combustion products from the bottom of the second hood used.

Because of the potential violence in conducting SCO-fuel reactions, a plastic safety shield should be employed when mixing reactants and conducting burn tests; such would protect the body and head from flying glass from the hood should the material react unexpectedly or with great violence.

HUMIDITY EFFECTS:

The effect of humidity on test outcomes and laboratory safety also merits attention. The US specification requires the relative humidity range to be $50\% \pm 10\%$. To obtain this range every day, requires in essence that the hood be inside a climate-controlled facility. The UN test protocol does not address relative humidity. Perhaps, the relevance of including a specification of the range of relative humidity for the UN test procedure should be addressed.

A few tests were conducted on rainy days to determine the effect of nearly 100% relative humidity

on the work environment and the test results. As to be expected, high humidity inhibited the combustion process. It was observed in the winter under conditions of low relative humidity that the KClO_3 -cellulose combustion reaction in some instances had caused the hood sash to "bang" against its channel. This "bang" was not present in the spring summer, or autumn time tests. Furthermore, that when conducting tests on the "dry" winter days, the combustion products and entrained reactants jetted from the hood into the laboratory more than in the summer during periods of high relative humidity.

Under conditions of high humidity either (1) the dry components as they are being mixed (in an open container) or (2) the components in the conically formed pile (if the pile is allowed to stand for an appreciable amount of time under ambient conditions before undergoing heating) would rapidly pick up moisture from the humid ambient air. Although the moisture added would be extremely small mass (percentage wise), there would be sufficient added moisture present to retard the reaction. The adsorbed moisture would promote agglomeration which would reduce the effective surface area to a certain extent depending on the level of humidity and the duration of exposure of the porous pile to it. More importantly, some of the thermal energy from the heater wire would be used to vaporize the freshly adsorbed moisture. This moisture would constitute a "heat" sink. Furthermore, the tiny pockets of steam formed from the vaporization of the moisture would provide inerting and thermal resistance, thereby retarding the rate of growth of the flame front. All of these factors would tend to diminish the flame temperature and the rate of production of gaseous combustion products.

A significant health hazard might occur while testing during a rainy day. The rain entrains the exhaust gas and smoke, forming a dense cloud which for some laboratory situations might be recycled into the building. Under quiescent conditions, including dry conditions, the dense cloud of combustion products might be recycled.

The UN procedure calls for a fume-extraction system which "should be suitable for the capture of toxic fumes" that enters the hood's exhaust stack. Using such a system would reduce any recycling problem. Although a scrubbing system to capture the fumes has definite merit, it will not eliminate jetting of combustion products into the work area if the hood is overwhelmed by a rapid reaction. Adding a

scrubber can add to the complexity of operations -it's another system that requires proper maintenance to avoid serious problems. Although a fume capture system increases costs, for some laboratory situations, to not use such a system would not be prudent.

*****FUTURE WORK**

As this study of very reactive compounds unfolded, it became obvious that important issues relevant to characterizing and assessing the hazards associated with oxidizers merited additional attention. Thus, an effort was made to characterize some important matters to address. Suggested future work relevant to the DOT mission is presented below.

It also became obvious that this work for the DOT had relevance to occupational health and safety not only in mining but in a wide range of other industries. It is internationally recognized that there are occupational health hazards associated with oxidizers. These health hazards appear in the manufacture, shipping, storage, handling, and use of SCOs in many different industries.

Heat Conduction Models to Predict Reaction Behavior for Mixtures of Oxidizers and Fuels

The combustion of mixtures of oxidizers and cellulose in conical or dome-shaped piles of small masses, say 20 to 60 grams, and even larger ones can be modeled mathematically. However, combustion is complex and modeling is only approximate at best, particularly where reaction kinetics are involved. The temperature distribution of the mixture during heating prior to ignition and just after ignition occurs can be approximately computed. However, such partial differential equation models could help in the analysis of accidents or incidents associated with various scenarios in the shipping, storage, and handling of SCOs. There is always concern about SCOs that might be accidentally contaminated by a fuel and subsequently undergo heating in an unconfined or semi-confined state.

EXPERIMENTAL CONDITIONS AND PHYSICAL DATA:

The conduction problem with heat input from the wire (150 watts) at the base can be formulated assuming that the wire is in the form of an annulus having an area equivalent to the lateral surface of a 24-cm length of AWG 18. For most of the UN tests with 30-gram mixtures, the length of the wire to which the 150 watts were applied was 30 cm; thus the power transferred to the pile was about 120 watts. Some power went into the Marinite® board (made from calcium silicate and reinforcing fiber) supporting the mixture mass. For some of the reactions open flaming commenced within five seconds and in some of

the more rapid reactions within about a second. Once the power is applied it takes several seconds for the 18 AWG wire to reach its full temperature as can easily be observed when applying current to a "bare" wire. Knowing the thermal properties of the wire and loss rate to the environment, one can determine a mathematical relationship for the growth in wire temperature with time ⁵.

As the reaction of the mixture of SCO and fuel proceeds, there are conductive, convective and - in some instances - significant radiative heat losses to the environment. Although these can be incorporated into the mathematical model, they add to the model's complexity.

In general one needs in addition to the three temperature dependent properties (conductivity, density, and specific heat) of the material other items: (1) the heat of reaction, (2) a kinetic rate law, and (3) appropriate probability distribution functions for the particle size of both reactants and their mixture. The heat of reaction and kinetic rate law are temperature dependent with the rate of reaction often being strongly dependent upon the temperature. The rate of the reaction is strongly dependent on the particle size of the solid reactants. Therefore, suitable particle size distributions that reflect both reactants needs to be incorporated into the kinetic portion of the model. The roles of the surface areas of the two reactants needs clarification. The mixture of SCO and fuel is bimodal. Whether the log normal distribution is appropriate needs further evaluation. Multiplying the kinetic reaction rate by the heat of the reaction gives the heating rate. As the reaction proceeds the mass of the reactants taking part increases as the reacting boundary spreads. This makes the model an expanding source type as far as internal heat generation is concerned.

The conduction model with heat input coming from the chemical reaction requires an estimate of the chemical reaction rate for the particular chemical model. Chemical models need to be hypothesized and confirmed for use with the heat conduction model. The use of the NASA Lewis CEA Code (PR 5, 6) for chemical equilibria is a useful tool in assessing the likelihood that the proposed model is appropriate.

⁵TEMPERATURE GROWTH IN AN ELECTRICALLY HEATED WIRE: The formulation of the partial differential equation for the conduction of heat in a thin wire heated by an electric current with radiative losses is addressed in Chapter 4 of Carslaw and Jaeger's book, Conduction of Heat in Solids, 2nd edition - see § 4.2, § 4.5, § 4.10, and § 4.12 (PR 11).

To facilitate a future effort in modeling of heat conduction for various solid oxidizers, thermodynamic information has been collected. From tabulated heats of formation, heats of reaction for various SCO - cellulose reactions were calculated. Because no tabulated value for the heat of formation of ammonium cerium nitrate could be found in the literature, its value was estimated. Chemical models were hypothesized for all the SCO-cellulose reactions pertaining to this study. The heats of reaction for all the SCO-cellulose chemical models pertaining to this study are provided in Appendix L.

Hazard Models to Predict Reaction Behavior for

Large Mixture Masses of Various Oxidizers and Fuels

Both the US and UN tests on classification of solid oxidizers address shipping hazards. They do not address storage issues that might be involved along the way. Both the US and UN tests are based on assessment of reactivities under small-scale conditions (sample mixture masses being 30 grams). Both the US and UN tests address the degree of hazard under open (unconfined) conditions - yet solid oxidizers usually are not shipped in an unconfined state. Both the UN and US tests do not address whether there is a mass effect that would enter in forecasting the relative reactivities and hazards associated with relatively large masses of solid oxidizers.

Differential thermal analysis (DTA) techniques are often helpful in characterizing materials and their decomposition temperatures. However, some of the commercially available units are only applicable to very small samples - 10 milligrams or less. Units to handle larger masses can be custom built. Nevertheless, useful information bearing on the properties of SCOs and on mixtures can be acquired via the DTA approach.

Sometimes in assessing oxidizer hazards, recourse is made to the concept of critical mass. It is thought that for some ongoing combustion reactions that more massive configurations of oxidizers provide greater thermal resistance, thereby facilitating both the accumulation of heat which raises the temperature and the rate of chemical reaction resulting in thermal runaway which in turn can lead to a transition from deflagration to detonation. To what extent the reaction mechanism is a function of the mass needs further clarification. In alternative wording, if for 30-gram test mixtures, compound A is more reactive than B, and B more reactive than C, the question to be asked for significantly larger test mixtures is whether it is possible for the order of reactivities to be different, say compound B more reactive than A ? What is needed is an assessment of the adequacy of small-scale SCO/cellulose tests to properly characterize the relative hazards associated with the shipping of solid oxidizers. Solid oxidizers such as ammonium ones contain hydrogen which can act as a fuel when an intense reaction gets underway. Ammonium oxidizers of sufficient fineness can act as molecular explosives, an example being ammonium

perchlorate. Some ammonium compounds are so unstable that they can not be shipped and are rarely synthesized. Solid ammonium chlorate is extremely unstable. Liquid ammonium chlorate can be made by reacting aqueous barium chlorate with aqueous ammonium sulfate; the driving force for this reaction is the rapid precipitation of barium sulfate. If the resulting aqueous ammonium chlorate were permitted to evaporate to dryness or be accidentally subjected to heating, or be contaminated with acid, then a most hazardous situation could result. Solid ammonium chlorate explosively decomposes at 102 °C. Evaporation can be done with the use of warm dry air or under vacuum conditions. Ammonium chlorate in an acidic medium forms chloric acid, HClO_3 .

It is conceivable that models could be developed to better predict the combustion times associated with much larger mixture masses. Effort should be spent in developing and validating larger-scale models. Data from intermediate-scale experiments would be of help while developing the models. Data, however, are lacking to support both the development and validation of such models. A lot of thought would need to be given to what larger size mixture mass is practical to work with and what size is needed for model development. The range of mixture masses in the initial tests could go up to a 1,000 grams. The effect of using fuels other than cellulose could also be evaluated. Such models could be evaluated by intermediate-scale burn tests in an open environment at a remote location with the essential environmental and safety issues addressed.

How to best characterize the duration of the burn would need to be addressed. Consideration should be given to determining the best type of data-logging instrumentation needed to conduct these large-scale tests to gain the information for realistic modeling. How the mixture is to be ignited needs to be considered. Electrical heater wire and chemical (JP5 fuel, hexane, heptane, etc.) approaches should be explored. If some combustion products should be monitored, then decisions need to be made on which ones to select. What kind of sampling system and sensors to monitor the production of specific combustion products needs attention. For some oxidizers, HCl formation should be monitored, for others NH_3 should be monitored, and for still others NO_x . In the case of carbonaceous fuels, CO should be monitored. In reactions with chlorates and perchlorates involving carbonaceous fuels the issue of whether

phosgene is produced merits attention. Thermodynamical studies on the likelihood of such a product being produced should be performed.

The selection of the oxidizers to be studied is most critical from a safety point of view. There are fewer problems with potassium nitrate than with other SCOs; ammonium nitrate would be a good candidate; potassium perchlorate is a possibility. There would be severe safety issues with using chlorates in even intermediate-scale studies. There are problems with using hygroscopic materials. There are mixing problems that are coupled to the reactivity of the mixture. The problem of a premature ignition during mixing and formation of the pile would need to be addressed.

The effect of partial confinement of the heated mixture could also be examined in the smaller-scale tests performed at a remote location. However, careful attention to safety is required before conducting these tests.

SCO Data Base for Information Retrieval and Data Analysis

A large amount of data on oxidizers [from over 800 tests], including video tapes, has been collected in this study and perhaps should be incorporated into a computerized data base. Such an effort in the related area of detonations is underway at The California Institute of Technology (Cal Tech). Cal Tech's web site [(IR 2) < http://www.galcit.caltech.edu/~jeshep/detn_db/html/ >] provides important data on detonations in graphical and tabular form with links to other references. Most importantly, this web site includes a search engine to facilitate retrieving data.

Information transfer and analysis for SCOs is best handled by a computer. Retrieving the information and processing it by noncomputer methods has been a tedious matter and should be simplified by use of a relational data base. Accessing the data remotely to perform analyses would be helpful. Being able to view short video clips of standard reference tests and select oxidizers and capture the information remotely for subsequent analysis has merit. To support this kind of information retrieval requires that a reliable database be established on a server.

The special video features provided in Windows NT 4.0, low cost SCSI hard drives, and low cost Synchronous DRAM now make inclusion of video in data bases an easier and more economical matter.

Data bases such as ACCESS and SQL by Microsoft are possibilities. Either an NT or UNIX server would facilitate remote access.

Laboratory Study of the Effects of SCO and Fuel Fineness, Reactant Composition, and Mixture Mass on the Burn Time

The objective would be to study the size effect of various SCOs and cellulosic fuels on the reactivity of the SCO/cellulose mixtures used in the UN Tests and develop suitable mathematical models relating at least combustion time, size distribution parameters, oxidant mass fraction, and mixture mass.

In conducting a SCO classification test it is conceivable that the result of using an oxidant powder having a much finer than typical size distribution could be a shift in the SCO's packing group assignment to a lower (more hazardous) classification value. SCOs can be produced, shipped, and used in a wide range of particle size. There are some pronounced differences in particle size distribution of the same chemical shipped by different manufacturers. Knowing the functional relationship among the particle size distributions of the SCO and fuel, mass fraction of SCO in the mixture, and the combustion times for 30-gram and less mixtures of SCO and cellulose is helpful in assessing the reactivity of a SCO that is to be shipped. Clearly, knowing the size effect on reactivity and having a practical way to apply it are important not only in the transportation of SCOs but also in their safe handling, storage, and use. Sometimes in the transportation and storage of hazardous goods, a slow combustion event may occur and lead to the generation of extremely toxic combustion products.

In some industrial applications, a mixture of two or more compatible oxidizers are used to achieve a desired effect. For example the use of ammonium nitrate with sodium nitrate helps to tailor the oxygen balance in emulsion type and other blasting agents. Strontium nitrate, which has a red coloration when intensely heated, is used with other nitrates to make tracer bullets. Strontium nitrate is used to slow down reactions (produce longer duration pressure pulses) involving either sodium nitrate or potassium nitrate with a fuel. [The boiling point of strontium nitrate is 645 °C; potassium nitrate decomposes at 400 °C; and sodium nitrate decomposes at 380 °C.] In the 1970's multiple solid chemical oxidizers were

incorporated into automobile safety air bags. Professor Alfred A. Schilt in his book, Perchloric Acid and Perchlorates, mentions (PR 12) specific examples of multiple solid oxidizers used in some air bags. Additional details from page 107 of his book are provided below.

“Potassium perchlorate is employed together with strontium azide and boron in a gas-forming composition which is suitable for the rapid inflation of automobile safety bags. Ignition of the gas-forming composition can be rapidly achieved in the event of an automobile collision by the use of ignition mixtures of boron, zirconium, aluminum, and/or magnesium with lithium perchlorate, sodium perchlorate, potassium perchlorate, ammonium perchlorate, and/or potassium nitrate.” [ORIGINAL SOURCE: T. Shiki, I. Harada, T. Hatrada, and M. Shiga. Japanese Patent 74,110,807 (1972)]

Over the years different formulations for the reactive system in air bags have been used. Various azides such as lithium, sodium, and strontium azide are used in air bags. Various mixes of perchlorates and nitrates along with reaction modifiers/inhibitors such as metallic oxides are put into the air bag unit. A wide range of fuels have been used in air bag units. These have included carbonaceous and/or metallic substances. The reaction rate is further tailored by selection of the appropriate particle sizes of the oxidizers and fuel components.

Understanding the reactivity of binary oxidizers with cellulosic fuels is important. Whether the effect of varying the ratio of mass fractions of the individual binary oxidants produces a linear or synergistic effect on reactivity merits attention. If binary SCOs are premixed prior to shipment or stored in a premixed state, an understanding of the relative reactivities of such mixtures would be an important matter to address.

A better understanding of the size effect on combustion times for the SCO/cellulose mixtures would help to identify shifts in packing group assignments and be of significant value in addressing related safety issues. Having a mathematical model that incorporates the combustion time, size distribution

parameters, oxidant mass fraction in oxidant/fuel mixtures, and mixture mass has merit.

The UN Manual of Tests and Criteria published important test data on mean burning times for SCOs [See Section 34.4.1.5]. Unfortunately, the data provided for 1:1 and 4:1 (oxidant:fuel) for the 15 SCOs does not give the particle size distribution parameters for the SCOs. If the particle size parameters were provided in the UN document for the 15 SCOs and if mathematical expressions relating combustion time, particle size parameters, and mass fraction of oxidant in SCO/cellulose mixtures for these 15 SCOs were readily available, the information would be most useful. Then laboratories would be provided with the proper basis for comparison of their test results with those published in the UN document.

Empirical mathematical type models would be a good step forward in developing mathematical models based on physical chemical principles that characterize the SCO/cellulose reactions for a wide range of conditions and chemical nature. The models would help to suggest mathematical functions to explore in developing physical - chemical models that can lend themselves for use in making hazard assessments. The models, by incorporating chemical reaction kinetics, could also be extended to provide useful data on fume production to address health related issues associated with dealing with unwanted oxidizer fuel reactions.

A model for the size effect based on data for at least three different sizes of cellulose would be useful. Studies with cellulose of particle size of about 500 and 1,600 μm to augment the data from the 25 and 125 μm cellulose could be performed. Such data would be useful in quantitatively relating the rate of combustion to the fuel's particle size parameters. Whatman Labsales, Inc. markets cellulose with average fiber length of 30 μm (CC-31), 200 μm (CF-1), and 125 μm (CF-11). Sigma Corporation markets cellulose with a mean length of 25 μm .

The intended statement of work is as follows.

1. Conduct a supporting literature study regarding combustion and modeling of SCO/fuel mixtures, the determination of packing groups, particle size analysis techniques for use with SCOs, particle size distributions relevant to characterizing SCOs, sampling devices for collecting fumes, and instrumentation for analysis of fumes. In addition, collect pertinent data on thermal decomposition of the

solid oxidants.

2. Obtain SCOs [KNO_3 , NH_4NO_3 , KClO_4 , KClO_3 , NaClO_3 , KBrO_3 , $\text{Mg}(\text{ClO}_4)_2$, and $\text{Sr}(\text{NO}_3)_2$] in various sizes.
3. Characterize particle distribution of the starting materials. For size analysis purposes different approaches will be considered - sonic sifter (screening), Coulter counter (if no incompatibility), Scanning Electron Microscopy (SEM), etc.
4. Pulverize the SCOs (except for potassium bromate) using a Retsch mill and various screen sizes (0.08, 0.120, 0.250, 0.50, 0.750, and 1.0 mm).
5. Characterize the particle size distribution of products pulverized in the Retsch mill and food processor.
6. Conduct preliminary SCO tests on select 30-gram or smaller sized SCO/cellulose mixtures, using such ratios as 3:7, 2:3, 1:1, 3:2, and 4:1, obtaining the means and standard deviations for the open flaming reaction times. Use two different sizes of cellulose. Identify stoichiometric oxidant-fuel ratios for SCOs. Conduct for the more energetic SCOs (those having very fine particle size) a few preliminary tests with mixtures having less than 30 grams - possibly 10 and 15 grams to start with. Perform a statistical analysis of the data. Then refine the test plan to identify test data needed for development of the model, taking into account statistical parameters from conducting replication tests.
7. Develop a general mathematical model involving the size distribution parameters for both SCO and cellulosic fuel, combustion time, mass fraction of oxidant, and one that takes into account the mass of mixture subjected to 150-watt heating. Perform a statistical analysis of the data.
8. Propose and/or conduct some additional validation tests for the SCO size and fuel size, combustion time, ratio of oxidant to fuel, and mixture mass model. The impact of surface moisture and relative humidity on the combustion time will be examined. If the model shows promise, then some effort should be devoted to identifying how the model should be extended.

Laboratory Study of the Reactivity of Liquid Oxidizers Mixed with Cellulosic Fuels in Open and Semi-confined Environments

The reactivity of liquid chemical oxidizers (LCOs) mixed with cellulosic fuel under open or semi-confined conditions is of importance in assessing their degree of hazard relevant to shipment. Although they could be studied under confined conditions, doing such requires special equipment and has some associated occupational safety and health problems that are mentioned in the UN test protocol which are very difficult to deal with. This method involves hand loading unstable explosive mixtures, which are liable to ignite spontaneously at room temperature, into a steel pressure vessel (pipe bomb) with a rupture disk. Once out of sight inside the vessel, the mixture could "cook off" without warning. When using nitric acid or perchloric acid, while the vessel is being closed, the operator could be sprayed with very fast moving metal fragments and hot acid. [The required reference substances are 50 % perchloric acid, 40 % aqueous sodium chlorate solution and 65 % aqueous nitric acid.] Wearing sufficient protective equipment would not allow enough dexterity for the procedure. It would be complicated and expensive to redesign this confined test method for remote operation.

The UN method procedure itself acknowledges the hazards: "... mixture which spontaneously ignites.", and "(if the mixture ignites during mixing or filling, no further testing is necessary.)" [See § 34.4.2 *Test O.2: Test for oxidizing liquids*, page 347, in "Recommendations on the TRANSPORT OF DANGEROUS GOODS: MANUAL OF TESTS AND CRITERIA (PR 2)]

Early work on the reactivity of LCOs had been performed by the USBM and in more recent times Japanese scientists had shown an interest in studying the reactivity of LCOs under open or semi-confined conditions. Kuchta, Furno, and Imhof in an experimental study of liquid oxidizers avoided some serious safety problems. This experimental approach involved the unconfined burning of liquid oxidizers. It was published (PR 13) in 1972 by Kuchta et al as Report of Investigations 7594, "Classification Test Methods for Oxidizing Materials."

Characterizing the reactivities of LCOs using similar test conditions somewhat analogous to those

used in the SCO studies but in a water solution with a containment approach, extra safety precautions to control splashing, and possibly a reduced mass of reactants, would provide a basis for comparing the dry and wet reactions and hopefully suggest a means of ranking the relative reactivities of LCOs, thereby avoiding the occupational safety and health complexities associated with conducting LCOs in a confined manner.

PRL proposes that a modified version of the Kuchta-Furno-Imhof procedure, published in Report of Investigations 7594, should be used. Some parts of the current UN Tests for Oxidizing Solids and Oxidizing Liquids would be incorporated. After perfecting the procedure outside a building and doing some exploratory studies with several candidate LCOs, the classification and reference standard tests would be conducted in an exhaust hood having proper wash down capabilities and a fume capture system.

The modified procedure would use an open 200 ml glass or stainless steel beaker with an inserted electric heating coil (equal to the UN CLO method specification). For sample temperature control (in the presence of high ventilation rates) electrical heating (such as a hot plate or heating tape) may be required. A 5 to 10 g quantity of UN specification cellulose would be added to the reaction vessel. A safety shield and containment system would be put in place. This may be in the form of a 6-inch diameter Pyrex glass pipe, with a side tee - holding a rubber septum. Then an equal mass of liquid oxidizer would be injected into the cellulose with a long hypodermic syringe, inserted thru the septum. The mixtures would be electrically heated (as in the CLO method) for 60 seconds. Inserted thermocouples (at the center and wall) would record temperature, and visual monitoring of burn time would be augmented with a video camera. The recorded burn time would be taken from when the power is switched on to when the main reaction ends. To determine the Packing Group (PG) the mean burn time (for 5 trials) would be compared with those of the normally used reference substances. These are:

- 50% perchloric acid (for PG 1),
- 40% sodium perchlorate solution (PG 2), and
- 65% nitric acid (PG 3).

Unfortunately, the latter standard poses a problem - it is extremely corrosive. To improve matters it is proposed that the 65% nitric acid reference standard be replaced with a less troublesome chemical. One such likely candidate is a 45% sodium nitrate solution. Naturally, the suitability of such a replacement would be evaluated experimentally.

Safe operation of any version of the liquid oxidizer test which includes perchloric acid (as a reference or test substance) will require the use of a specially constructed perchloric acid laboratory exhaust hood. This is detailed (**PR 14**) in the U.S. Department of Interior Employees Accident Prevention Handbook (revised January 1972, pp. 117-123). Section 714 (pp. 122-3) specifies type 316 stainless steel construction and integral internal wash down design:

- "c. It is important that all parts of the system, including the exhaust fan, ductwork, and hood, be supplied with flushing devices for wash down purposes."**

The intended **STATEMENT OF WORK** is as follows:

1. Conduct a supporting literature study regarding combustion of CLO/fuel mixtures and the determination of packing groups.
2. If proper exhaust hoods (with fume capture system) are not in place, then they would have to be designed, purchased, and installed.
3. Obtain the LCOs: HClO_4 , HNO_3 , NH_4NO_3 , NH_4ClO_4 , KNO_2 , KClO_3 , NaNO_3 , NaNO_2 , NaClO_3 , and NaClO_4 .
4. Analyze LCOs for strength, purity, and water content through contract analysis services.
5. Set up prototype unconfined test procedure and perfect the method.
6. Conduct tests with reference substances, including replacement candidates for nitric acid, and analyze the results statistically.
7. Classify test solutions, determine PG values, compare the PG results with those determined by the confined method. Only a few tests will be conducted with nitric acid.
8. If necessary, select additional liquid oxidizers that are close to the PG boundaries for further validation of the unconfined test method.
9. Finalize the test procedures.

Some appropriate comments on equipment and procedural matters that take into account the occupational safety and health aspects are as follows.

The safety of personnel and environmental concerns (air emissions and hazardous waste) can best be controlled with proper wash down hoods having toxic fume capture capability (as mentioned in the UN test procedures for SCOs). The wash down features include: built-in sprinklers, a sink with valving to permit collection in a holding tank, steam capability to facilitate loosening of deposits, and a hand-directed

spray to wash down the surfaces not cleaned with the automatic sprinklers. Special personal protection gear is required during the wash down operations. It is required that such hoods be equipped with a three-speed exhaust motor blower. The exhaust ducts will need to be custom made from 316 stainless steel or equivalent material; stainless steel plumbing will be needed with both hood drains having a two-way valve for collecting waste material in a tank or sending nonhazardous water to the sewer. A feature to prevent an overflow problem with each collection tank is required. A level indicator should be connected to each collection tank. The overflow could be avoided through the use of a valving arrangement. In order to work safely with the LCOs, special respiratory equipment will be needed that will not impede the work effort. Other required laboratory items would include equipment for heating and temperature monitoring, preparation of saturated solutions, video recording, and safety shielding. It is imperative in working with hazardous materials or dangerous goods and in conducting potentially hazardous operations that there be a total commitment to occupational safety and health in the research environment. The proper equipment simply must be made available before such work commences.

Preferably at the research proposal stage and especially before a project with dangerous goods is initiated or agreed to be conducted, some questions ought to be addressed to management's satisfaction:

(1) What are the safety and health concerns and issues? (2) What safety and health measures need to be taken and equipment purchased? and (3) Will higher level management provide the necessary financial resources to ensure that an occupationally safe and healthy work environment exists if it is decided to proceed even though the current funding does not adequately address the safety needs? What the definition of management's satisfaction is merits clarification. It might not only mean to the satisfaction of the (1) Chief Medical Officer, (2) Health Physicist, or (3) Chemical, Biological and Radiological Safety Officer but also to the satisfaction of either the Research Director or his/her Deputy depending on the organization. Although to some this might seem too strong to be applied to research, it is essentially the approach adopted by the chemical manufacturing and insurance industries in Great Britain following its biggest chemical disaster in the 1970's. In the UK at the proposal stage for plant design the health and safety issues must be addressed before the work is authorized to proceed.

***CONCLUSIONS

1. The standard deviations (based on sample size of 5) of the mean burning times for the UN tests were generally less than the standard deviations (based on sample size of 3) for the US tests.
2. Using the UN procedure with UN published example burning times of 100 seconds, 54 seconds, and 4 seconds yielded 30 out of 38 classifications (79 %) as being the same as the published UN classifications. Six of the "DISAGREEMENT" cases were associated with nitrates. (The 100-s value corresponds to the 3:7 mass ratio; the 54-s value corresponds to the 2:3 mass ratio; and the 4-s value corresponds to the 3:2 mass ratio.)
3. The mixture having a 3:2 mass ratio of KBrO_3 to cellulose with a SCO particle size range of 150 μm to 300 μm when burned by the UN test procedure yielded a mean burning time 10 seconds greater than the UN published example value. Possibly because of this difference in mean burning time, classifications using the UN KBrO_3 reference SCO with a particle size range of 150 μm to 300 μm yielded only 11 out of 38 classifications (29 %) as being the same as the published UN ones.
4. When the size range of less than 150 μm was used for the 3:2 mass ratio, a mean burning time 1 second greater than the UN published example value was achieved. Although good agreements with the burning times for the 3:7 and 2:3 mass ratios for the less than 150 μm particle size range of KBrO_3 were not achieved, using the UN procedure with a KBrO_3 as a reference yielded 27 out of 38 classifications (71 %) as being the same as the published UN ones.
5. The tests performed using KClO_3 as a proposed reference standard with a particle size range of less than 300 μm and mass ratios of 1:7, 1:5, and 2:1 yielded 29 out of 38 classifications (76 %) as being the same as the published UN ones. Six of the "DISAGREEMENT" cases were associated with nitrates.
6. Packing Group classifications, based on the US test procedure and PRL experimental data using KBrO_3 , KClO_4 , and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ standards of 300- μm -or-less particle size, yielded only 3 out of 14 classifications (21 %) as being the same as the published US ones.

7. Packing Group classifications, based on the US test procedure and PRL experimental data using a set of KClO_3 / basswood standards (11 seconds for a 2.53:1 mass ratio; 50 seconds for a 3:10 mass ratio; and 80 seconds for a 2.2:10 mass ratio) with the chlorate being 300- μm -or-less particle size, yielded only 7 out of 14 classifications (50 %) as being the same as the published US ones.
8. There is a need to identify a statistical criterion for rejection of an outlier and establish criteria to determine whether additional tests are needed.
9. The analysis of the experimental data and consideration of health properties of SCOs provides an adequate basis to advocate that the US adopt a "refined" version of the UN test protocol for SCOs which entails among other things replacing the three potassium bromate / cellulose mass ratios used as standards with three potassium chlorate ones. If it were decided that in the "interim" or "transitional" time period for adopting the UN test protocol that the US test protocol would be utilized, then some key changes should be made; these include replacing the current set of three reference standards (potassium bromate, potassium perchlorate, and ammonium persulfate) with potassium chlorate at three different oxidizer-fuel mass ratios, and increasing the sample size number to five. If the sawdust were replaced with cellulose of the fineness used in the UN test protocol, then there would be only minor differences between the refined US and UN test protocols.
10. Of the four wire sizes examined, AWG-18 wire with resistance, 1.33 Ω/m , and diameter, 1 mm, was the most durable during the tests and yielded results not much different from preliminary results using thinner wire.
11. It was found that construction of the conical pile by pouring the mixture onto the heater wire at the angle of repose of the mixture simplified the procedure without adversely affecting the test results.
12. The determination of the end of burning of the mixtures was an exceedingly subjective decision for many of the tests. For the more rapid reactions with open flaming, it was relatively easy to measure the burning time. For the slower reactions with only smoking and no flaming, it was

often very difficult. The use of video recording equipment improved the accuracy of the burning time determination.

*****RECOMMENDATIONS**

1. To lower the standard deviation and help to better identify outliers, the US procedure for classifying SCOs should be based on performing at least **5** tests at the **1:1** level and at least **5** at the **4:1** level.
2. Some consideration should be given to evaluating whether the **t-test** should be employed in SCO test protocol to compare means for material undergoing classification with those for reference standards. Applying hypothesis testing techniques, when the mean burn time for the material being classified is close to the demarcation time between Packing Groups, would be advantageous and desirable. This entails (1) determining whether a correct statistical basis exists for comparing the SCO means by use of the **t-distribution** and (2), if so, what are the appropriate levels of significance (α) to use.
3. The US procedure could be significantly improved by replacing the **< 1,600 μm** sawdust with cellulose of particle size having a fiber length between **50** and **250 μm** and a mean diameter of **25 μm** similar to that used in the UN test procedure and using a set of potassium chlorate reference standards of appropriate mass ratios of SCO to cellulose, thereby lowering the standard deviation and eliminating the use of a human carcinogen as a standard. Special consideration should be given to implementing this if it is decided to retain the US test protocol.
4. The criteria indicating the end of combustion in both the US and the UN procedures are highly subjective. For this reason, a more quantitative criterion should be specified for the end of combustion. Different possibilities, such as the peak temperature in the pile as recorded from a thermocouple, pyrometer, or heat-flux gauge, should be evaluated.
5. The pile should be formed at its angle of repose to reduce the possibility of a change in its form with possible scattering during burning which could result in incomplete burning.
6. Because of the potential violence in conducting SCO-fuel reactions, a plastic safety shield should

be employed when mixing reactants and conducting burn tests; such would protect the body and head from flying glass from the hood should the material react unexpectedly or with great violence.

7. For health reasons, because KClO_3 is not carcinogenic, it would be better to use KClO_3 than the human carcinogen, KBrO_3 , in preparing the set of reference standards for the UN tests.
8. To reduce the tendency of the pile to scatter and maximize the amount of SCO participating in the burn, use of restraining band of cylindrical shape around the conical pile should be investigated. Also different locations in the pile of mixture for the heater wire should be investigated. One way to accomplish this might be to place the heater wire higher up in the pile after the pile has been formed. This implies that the effect of varying the shape of the heater wire on burn time be investigated.
9. For some laboratory configurations, to help prevent jetting of gas and smoke from the hood into the laboratory, it recommended that the test surface be elevated at least 10 cm above the bottom of the hood.
10. For small hoods at least 0.8 m^3 in volume, the total mass of the mixture should be reduced to about 20 g or less to enable testing of the rapidly reacting Packing Group I SCOs without having the combustion products jet from the hood into the laboratory.
11. At the start of a test the timers should be electrically coupled to the start of current through the ignition source. When tests are performed, it is easy at times to not properly synchronize these start times by relying only on audible information transfer between the laboratory personnel conducting the tests. A visual indication of the start of the ignition current should be positioned in the field of view of the video recording device to be made part of the permanent record.
12. The UN Manual of Tests and Criteria published important test data on mean burning times for SCOs (See Section 34.4.1.5). Unfortunately, the data provided for 1:1 and 4:1 (SCO : fuel) ratios for the 15 SCOs does not give the particle size distribution parameters for the SCOs. If the particle size parameters were provided in the UN document for the 15 SCOs, the information

would be most useful. Then laboratories would be provided with the proper basis for comparison of their test results with those published in the UN document. A better understanding of the particle size effect on combustion times of the SCO-cellulose mixtures also would be of value in analyzing the safety status of shipping situations.

13. The use of an integral wash down hood made from type 316 stainless steel of sufficient volume, preferably at least 2 m³, would facilitate matters and reduce laboratory contamination with toxic, carcinogenic, or otherwise difficult chemicals. Ideally, the use of two sufficiently large exhaust hoods made from type 316 stainless steel of the wash down type next to each other in the laboratory would reduce the general contamination of the laboratory during the preparation (grinding, sieving, and weighing) of SCOs, while conducting the combustion test, and during the clean up operation following the test. One hood would be for containing the equipment for grinding, sieving, and weighing of chemicals - this would be appropriate in the grinding of large quantities of oxidizers or in handling the more "difficult" ones. The other hood would contain the support apparatus for the reaction mixtures and the products of burning.
14. A review of the existing domestic and international research literature on the physical chemical aspects of ammoniated oxidizers bearing on safety issues should be conducted to help focus on research needs. Such a review and the subsequent research findings would be of value to those concerned with the shipment, handling, and use of solid oxidizers.

***ACKNOWLEDGMENTS

The authors acknowledge Dr. Charles P. Lazzara, supervisory research chemist; Dr. Isaac A. Zlochower and Alex C. Smith, research chemists; Robert A. Franks, electronics engineer; Barbara Heirendt, environmental scientist; Henry J. Kellner, safety and occupational health officer, and Carl T. Ornot, industrial hygienist, for providing general assistance throughout the course of the investigation. Special thanks go to the four chemists - Drs. Robert Chaiken, Charles Lazzara, Frank Perzak, and Isaac Zlochower - for their intensive review of the report and their many suggested improvements.

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8. <http://ATSDR1.ATSDR.CDC.GOV:8088/> (Center for Disease Control and Agency for Toxic Substances and Disease Registry's 1995 full priority list of hazardous substances)

*****APPENDIX A:**

Graphs of Hood Air Flow Parameters versus Sash Opening Height

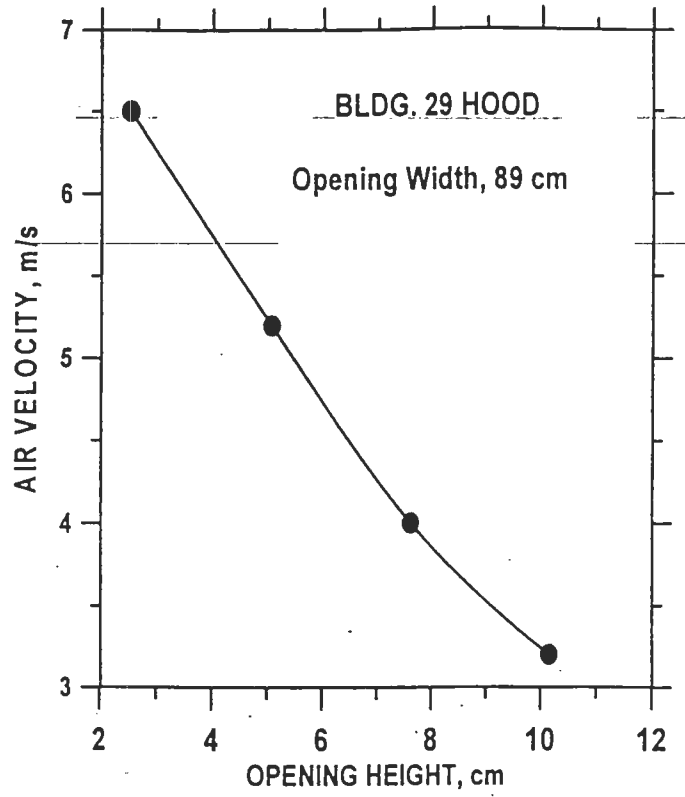


Figure A-1. Air velocity into building- 29 hood versus height of sash opening

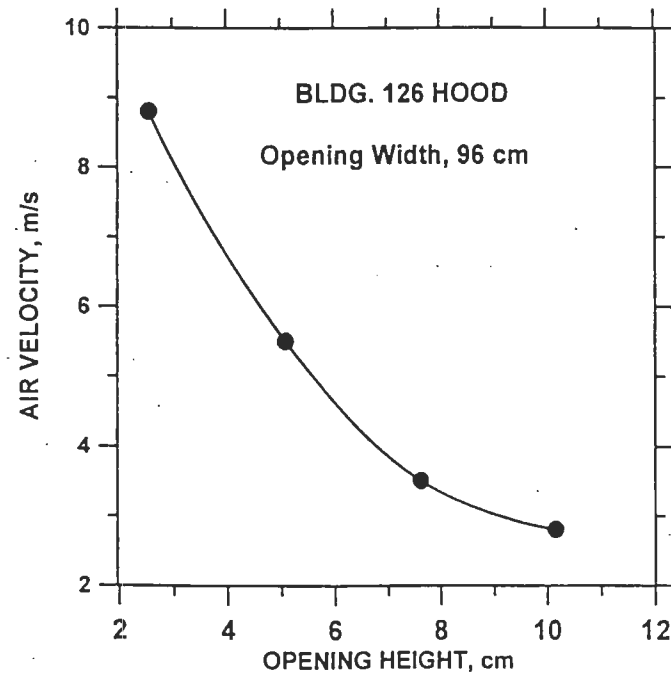


Figure A-2. Air velocity into building-126 hood versus height of sash opening

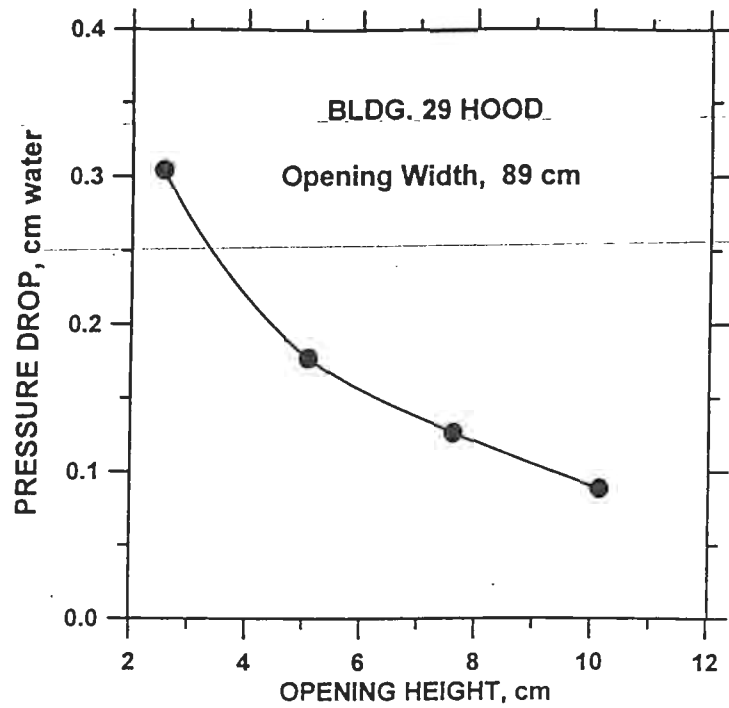


Figure A-3. Pressure drop into building-29 hood versus height of sash opening

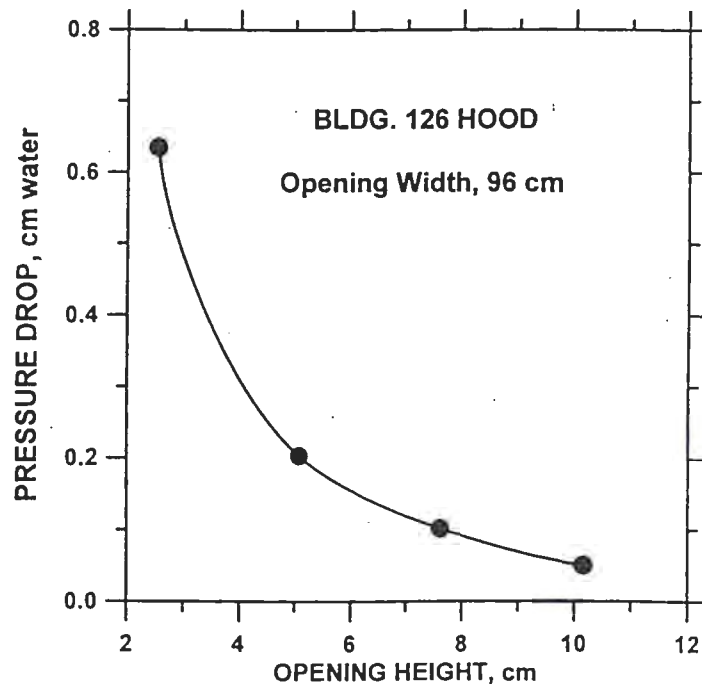


Figure A-4. Pressure drop into building-126 hood versus height of sash opening

*****APPENDIX B:****Experimental Hazards of Solid Chemical Oxidizers**

Sample Preparation by Grinding and Sieving

There are a number of considerations involved when trying to produce hundreds of grams of fine powder in a known particle size range for testing. Motorized grinding and sieving equipment, even though more expensive, is more practical than extremely time consuming hand methods. Preferably all wetted parts of the equipment should be made of corrosion resistant material (glass, plastic, aluminum, or stainless steel). Carbon steel parts can cause rust contamination. Brass sieves should be avoided. A single processing step by a grinder or pulverizing mill with an integral outlet sieve is much preferred. With this arrangement, the suspended ground particles are blown through the sieve before they have a chance to agglomerate. It is difficult to hand sieve powder (below 150 μm size) when the particles have clumped together, especially if the chemical is hygroscopic (such as sodium and ammonium salts) and the air relative humidity is above 50%. The ground and sieved chemical should be used as soon as possible, sealed in an air-tight container, or stored in a desiccator cabinet.

Safety Planning

Before purchasing hazardous chemicals (such as SCOs) for testing, Material Safety Data Sheets (MSDS)s and other relevant safety literature should be reviewed. However, it should be noted that MSDSs are not always current. Although potassium bromate has been known since January 1, 1990 by the state of California to be a carcinogen, its carcinogenicity status has not been updated in some of the MSDSs prepared in the United States. Potassium bromate's carcinogenicity has been recognized in the State of California, Canada, Japan, the United Kingdom, and the other European Common Market countries; and its use is restricted in some countries (Japan, Canada, and the UK). [See the UK's MAFF web site (IR 3) < <http://www.maff.gov.uk/food/infosheet/1993/no02/02bread.htm> > for the chemical analysis procedures for and results of a survey on residual bromates in British foods.]

The most extensive and current American list of human carcinogens is posted on the State of California's web site maintained by California's Office of Environmental Health Hazard Assessment, a

subdivision of the Environmental Protection Agency. Hexavalent chromium was declared to be a carcinogen by the State of California on February 27, 1987. It was included in the first list of carcinogens published as a consequence of Proposition 65. The most current list of chemicals known to cause reproductive toxicity is also posted on the State of California's web site. As of December, 26, 1997, about 550 carcinogenic and reproductive toxicant compounds appear in the State of California's list.

[See (IR 4) < <http://www.calepa.ca.gov/oehha/docs/12971st.htm> > for the December 26, 1997 listing of known carcinogens and chemicals having reproductive toxicity.] Detailed technical information - on the determination process for carcinogenic and reproductive toxic substances, allowable risk levels, etc. - and relevant research findings bearing on chemical safety are published on-line by "Prop 65 News."

[See (IR 5) < <http://www.prop65news.com/pubs/p65news/issues/> > .] Detailed discussions of the legal meaning of "Clearly Shown" with respect to carcinogenic and reproductive toxicant compounds were prepared by Charles Ivie, John Kronstadt and Gary Roberts and published in "Prop 65 News", July 1997, Vol 11, No. 7 (Part I) and "Prop 65 News", August 1997, Vol 11, No. 8 (Part II). [See (IR 6) < <http://www.prop65news.com/pubs/p65news/issues/9707/970714.html/> > for Part I and (IR 7) < <http://www.prop65news.com/pubs/p65news/issues/9708/970811.html/> > for Part II.]

The means and costs of disposal should be determined in advance -- especially since some of the SCOs are highly toxic or carcinogenic. Determine the proper facilities, equipment, materials, and methods needed to safely handle these chemicals. This includes possibly using remote work areas equipped with laboratory exhaust hoods with integral sinks and fume extraction equipment. The proper personal protective equipment should be available. Eye and body wash equipment and equipment to contain spilled chemicals should be nearby.

Chemical Reactivity

Of special importance is the decomposition temperature of SCO. Sometimes the information on thermal decomposition is provided in handbooks. However, when the data is lacking, the use of a differential thermal analyzer can be of considerable help. Differential thermal analysis (DTA) techniques are especially helpful in characterizing materials and their decomposition temperatures.

When SCOs and fuels are combined in specific ways, the resulting mixtures can be explosive causing injury to personnel and damage to facilities and equipment. A number of factors affect the sensitivity (ease of ignition) of a SCO-fuel mixture. The sensitivity increases as the particle size and water content (in the mix and the laboratory relative humidity) are decreased. The sensitivity often reaches a maximum when the SCO-fuel ratio is approximately 4 to 1 by mass or near stoichiometric (ideally balanced so there is enough oxygen available to burn all the carbon in the fuel to CO_2 and H_2 to H_2O). A fourth factor is the chemical stability of the SCO itself. Some mixtures of SCOs and fuels are extremely reactive, to the point of being explosive and possibly undergoing spontaneous ignition at room temperature -- especially when dry (static-electric arc sensitivity), reduced to a fine particle size, and subjected to friction (as in mixing).

Chlorates are the most notorious example, especially if they become contaminated with acid, acidic salts, or ammonium salts. The degree of reactivity can be judged for a given mass of mixture by the total burning time. For example, once ignited, chlorate mixtures can be completely consumed within a few seconds. In fact, if ignited from the bottom, the mixtures may not stay in a pile. The gas can be generated so rapidly that the particles above it are levitated and ignited producing a dust explosion.

Increasing the mass of mixture escalates the burning rate via self-confinement. Gas and heat are better contained increasing the temperature and pressure. The total heat produced is also increased.

For these reasons, when testing a mixture of unknown burning rate, sensitivity, or reactivity, it is safer to progress from small quantities, such as 2 g, before burning larger quantities, such as 30 g. Use published burning rates as an initial guide.

Some SCOs become unstable in a finely ground state; ammonium perchlorate $[\text{NH}_4\text{ClO}_4]$ ground to less than $45\ \mu\text{m}$ can be detonated. The ease of detonation is increased when metal or other impurities are present. Alfred A. Schilt in his book, *Perchloric Acid and Perchlorates*, writes (PR 12) "It is both reasonable and wise to assume that all organic perchlorate and most heavy metal perchlorates are capable of explosive decomposition under certain conditions."

Some SCOs when contaminated with a slight amount of acid become very reactive, an example

being potassium chlorate [KClO_3] which in combination with acid gives HClO_3 , a highly reactive compound.

Laboratory Exhaust Hoods

The location and height of the hood exhaust pipe should be considered in relation to other nearby personnel. If burn tests are conducted in the hood, the exhausted combustion fumes could recirculate (due to down drafts or temperature inversions). This can be a problem when burning chemicals such as ammonium persulfate that generates very noxious fumes such as SO_2 . For these chemicals, as well as carcinogens, a fume scrubber may be needed on the exhaust pipe. The best design also includes a perchloric-acid-type, wash-down hood with integral trough sink and cup sinks with faucets.

Very fast burning (2 seconds or less) mixtures may require a larger volume hood (6 ft wide) to contain the combustion fumes. Otherwise, the smoke will jet out from the hood and contaminate the room. The directed energy from the explosive like reaction provides sufficient momentum for some of the reaction products and entrained unreacted material to overcome the momentum of the air stream entering the hood. It is this violent process which accounts for the undesirable jetting of material out into the laboratory work area. For the first trial of a mixture of unknown burning time, the operator should initiate the burning from a safe location which for some laboratory situations might be outside the room containing the hood. It is advisable to use plastic barricades around the sample in the hood.

All dust-producing operations including weighing should be done in the hood. Dust contamination of the personnel and room can be produced in various ways. Grinding and mixing produce a lot of fine dust which can back stream out of the hood (while it is running) into the laboratory (especially if the hood lacks a bottom air foil). Contaminated hands and utensils, removed from the hood, can contaminate the room. Therefore, it is advisable to rinse gloves, hands, and utensils inside the hood. If the hood lacks water and a drain, use a catch tray and pipe water in or use wash bottles. To prevent cross contamination, hood surfaces should be cleaned with wet paper towels before switching to a different SCO.

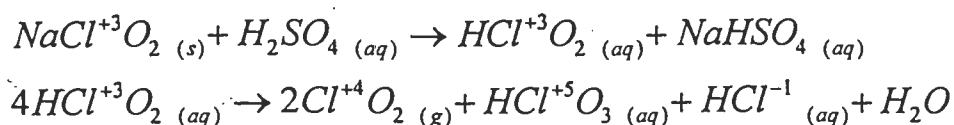
Health Hazards and Personal Protective Equipment

All of the oxidizers are irritants. It only takes a small amount of SCO to cause a serious eye ailment. The transference of a small mass of SCO, that equivalent to the volume of a pinhead, from a contaminated laboratory surface to the face near the eye can result in a severe irritation of the eye. Fine dust entrained in the air during either the handling of SCO or conducting energetic tests can be deposited on the face, causing an eye irritation that can persist for days. Therefore, eye protection and proper exhaust hoods are essential. Clearly, special care must be taken in the handling of SCOs, in controlling laboratory contamination, and in cleaning personal protective gear following the handling of SCOs.

Some SCOs are human carcinogens, such as chromium trioxide [CrO_3] and potassium bromate [KBrO_3]. The health hazard of chromium trioxide (often referred to as Chromium -6 or hexavalent chromium) and its impact on humans and animals in a community in California have been well documented. Chromium trioxide is listed as 15th on the Department of Health and Human Services' List of Top 20 Hazardous Substances compiled by the Agency for Toxic Substances and Disease Registry (ATSDR). ATSDR's 1995 full priority list of hazardous substances includes 275 chemicals. (See ATSDR's web site (IR 8) < <http://ATSDR1.ATSDR.CDC.GOV:8088/> >.)

Some SCOs are corrosive, such as chromium trioxide [CrO_3] with designation of Class I. **The human skin in a slightly moist state after coming in contact with chromium trioxide undergoes harsh attack. Within a short period of time the total skin layer can be destroyed with the SCO entering the bloodstream as a carcinogen.**

Some oxidizers generate hazardous gases upon contact with acid. **Calcium hypochlorite [$\text{Ca}(\text{ClO})_2$], a bleach, gives off chlorine gas upon reacting with acid. Sodium chlorite [NaClO_2] gives off chlorine dioxide, a poisonous gas, upon contact with acid.** Therald Moeller in his textbook, Inorganic Chemistry, provides (PR 15) a two-step reaction mechanism to account for the formation of chlorine dioxide from the acidification of chlorites. The reaction sequence is as follows:



Some SCOs are poisons, such as potassium iodate [KIO_3], potassium periodate [KIO_4], barium nitrate [$Ba(NO_3)_2$], and barium chlorate [$Ba(ClO_3)_2$] as noted in chemical vendors catalogs. **Because most of the SCOs are soluble in water, the toxic and carcinogenic ones are best handled in a wash down type hood in order to control laboratory contamination.** Clearly, no storage of food or consumption of food, including beverages, should take place in a laboratory area where contamination is possible. **Some SCOs are sensitizers that affect the immune system, such as potassium perchlorate [$KClO_4$] as noted on the manufacturer's label placed on the container.** Some oxidizers when reacted with fuels give off toxic gases such as sulfur dioxide [SO_2]. For example, ammonium persulfate [$(NH_4)_2S_2O_8$], one of the less reactive SCOs, produces sulfur dioxide when reacting with sawdust or cellulose. The reaction of ammonium persulfate with sawdust (in a 30-gram mixture) often lasted for more than eight minutes. The dense sulfur dioxide can be recycled into the laboratory work area under certain conditions. Care, therefore, must be taken in choosing a laboratory location for an exhaust hood. Having a scrubber system can be of particular value in dealing with the combustion products from SCO / fuel reactions that are conducted in a laboratory hood.

To help protect against dust and burns from accidental ignition of SCO-fuel mixtures, the following equipment is recommended; safety glasses, chemical splash goggles, face shield, gloves, and flame-resistant laboratory coat. The gloves should be rubber or plastic lined with cloth. Rubber or plastic gloves without liners can melt and stick to the skin. Gloves with a cloth exterior are a fuel, and when they absorb a SCO, they become a flammable mixture. A respirator should be worn anytime the face is exposed to SCO-dust producing operations. The eyes are most susceptible to injury from the corrosive effects of SCO. A single soluble SCO dust particle can react with the moist eye tissues and release concentrated corrosive gases and acids. Therefore, safety eye wash fountains, etc. should be close at hand and

checked frequently. After testing it is important to wash dust-contaminated safety glasses, goggles, etc. and to not touch the eyes or face with contaminated hands or gloves. Sink faucet handles should also be frequently cleaned.

Safe Handling Procedures

To reduce the effects of possible explosive fragmentation risk to personnel, only dry paper cups (coated or uncoated) or cardboard containers should be used for mixing and storing. Styrofoam cups because of their strong tendency to hold a static charge must be avoided. Cups made of material that upon fragmentation would cause harm must be avoided. One needs to watch out for the reactivity of SCO with paper if the paper is damp or wet. Wooden tongue depressors are useful for stirring. Potassium nitrate is a useful SCO for practicing mixing and handling techniques. It has moderate reactivity, is relatively easy to grind, is not hygroscopic, and is not highly toxic. Plastic rather than glass funnels are preferred when forming conical piles. To reduce friction, plastic rods should be used to push mixtures through funnels. However, it is better to pour the mixture to form the pile at its natural angle of repose. When working with mixtures, partially lower the glass hood sash to below the level of the SCO. The glass sash will then function as an additional shield. When working with unknown or very reactive mixtures, one should use plastic barricades around the mixtures in the hood. Mixtures should not be stored but rather consumed shortly after they are made. Reused utensils and gloves should be washed with water in the hood, if possible, and dried before being used for a different SCO. **It is of utmost importance to prevent chlorates from being contaminated with ammonium salts.**

Good safety practices are also required following conducting tests. **To prevent fires, any items contaminated with SCO and any post-combustion residues should be treated with water before being discarded into wastebaskets.** These materials should be emptied into an outside trash container, preferably away from buildings to further minimize the possibility of a spontaneous combustion problem, when the operators complete the work for the day.

*****APPENDIX C:**

Procedural Matters

Details of Experimental Procedure

1. Measure the velocity of air into the ventilating hood at the middle of the sash opening when the glass is fully open. The velocity of air into the hood should be at least 25 m/min for slow reactions and, preferably, between 7 and 10 m/sec for fast reactions.
2. Put on a facial dust mask or respirator with safety goggles.
3. If using sawdust as the fuel, sieve the fuel inside the ventilating hood through a 1.6 mm sieve. Discard or store the large sawdust particles.
4. Put the sieved fuel into an open inert and heat resistant container.
5. Put the container inside a 105 °C oven for drying for 4 hours.
6. After the fuel has dried, put the fuel into a
7. Put on plastic gloves and a respirator.
8. Inside the ventilating hood, sieve the SCO through a 300 μ m sieve.
9. Inside the ventilating hood, put the sieved SCO into an open inert and heat resistant container.
10. Put this container inside a 65 °C oven for 12 hours - if the material is hygroscopic an inert dry gas flow is needed. (There are problems with drying deliquescent materials in ovens - often it is better to store the material in a desiccator with a "fresh" drying agent .)
11. Inside the ventilating hood, pour the SCO remaining in the sieve stack through a large funnel into a labeled jar.
12. After the SCO has dried and before removing it from the oven, put on plastic gloves and a respirator.
13. Put the dried SCO into desiccator used only for SCOs.
14. Put on a facial dust mask or respirator with safety goggles. With a balance inside the ventilating hood weigh 15 g of dried fuel into a small labeled paper cup for a 1:1 mixture of oxidant to fuel or weigh 6 g of fuel into a cup for a 4:1 mixture of oxidant to fuel.
15. Put the cup with the weighed fuel into the fuel desiccator.
16. Put on plastic gloves.

17. Inside the ventilating hood weigh 15 g of dried SCO into another small labeled paper cup for a 1:1 mixture of oxidant to fuel or weigh 24 g of SCO into a cup for a 4:1 mixture of oxidant to fuel.
18. Put the weighed SCO into the SCO desiccator.
19. Set two rows of refractory bricks or equivalent supports near the back of the hood. Set a large porcelain (or equivalent) tray on top of the bricks. Put a refractory board in the middle of the porcelain tray. Lay a 6-inch square of a disposable refractory sheet, such as Fiberfrax (ceramic aluminosilicate fibers, $\text{Al}_2\text{O}_3\text{-SiO}_2$, from John Mansville Co.), on the refractory board. Since Fiberfrax is an irritant and the IARC has classified ceramic fibers as being a possible human carcinogen (Group 2B), gloves and a respirator should be worn when handling and cutting this material.
20. Position the appropriately configured ignition wire on the sheet with laboratory clamps.
21. For a US test, aim an optical pyrometer at the ignition wire. Set a power supply current to give a wire temperature of 1000°C , and record the current flowing through the wire. (For the majority of our tests, the current was set to 19.4 amps for 150 W of power dissipated in 30 cm of AWG 18 wire with a composition of 80% nickel and 20% chromium.)
22. Switch off the power to the wire.
23. Set up video recording equipment that has slow-motion play-back capability.
24. Put on a respirator and safety goggles.
25. Remove the fuel and SCO cups from their desiccators and place them in the ventilating hood.
26. Inside the ventilating hood, pour the weighed fuel into a large paper cup (approximately 750 cc in size).
27. Put on protective gloves, lower the hood glass sash below eye level, and pour the weighed SCO onto the fuel in the large paper cup.
28. Store the small empty cups in their respective desiccators for use that day with the same materials, or rinse with water and discard.
29. Using a tongue depressor or equivalent safe tool, carefully mix the ingredients inside the large

cup until the mixture is uniformly mixed - usually this takes one minute with vigorous mixing. (For either rapid reactions or those of uncertain rapidity, plastic barricades should be placed around the sample mixture prior to its ignition.)

30. Pour the contents of the large cup onto the center of the ignition wire.
31. Discard or store the large cup for later use that day with similar mixtures.
32. Lower the hood glass sash to about 1 inch above the bottom of the hood. (In the case of extremely rapid reactions or those of uncertain rapidity, to avoid injury from shattering of the hood's sash glass, one should work behind a plastic portable barricade.)
33. Set two stopwatches to 0 s.
34. Record the temperature and humidity in the ventilated hood.
35. Start the video recording equipment -- making sure a timing device with seconds indication is superimposed on a corner of the viewing screen.
36. Switch on power to the ignition wire and start both stopwatches.
37. When ignition occurs, stop one of the stopwatches, and, for the US procedure, turn off the current to the wire.
38. When the main combustion of the mixture ceases, stop the other stopwatch.
39. Stop the video recording equipment, rewind the video tape, and verify the burning times.
40. Record the parameters identifying the test -- including the ingredients and quantities in the mixture and the times of events (see Appendix D).
41. After about 5 min and when the air inside the hood is clear, put on gloves, the respirator, and raise the glass shield to remove the refractory sheet and any residue. (With 1:1 mixtures, significant residue may be left and pouring about 5 cc of water on this residue will hasten its cooling.)
42. Carefully remove the ignition wire from the residue. Scrape residue from the ignition wire into a side of the large porcelain tray and reshape the wire for another test.
43. Put the used refractory sheet into a trash container. Use a brush or a paint scraper to clean

dispersed residue into a side of the porcelain tray for later disposal.

44. At the end of a test series or at the end of each day, pour the residue from the porcelain tray into the trash container and moisten to reduce the possibility of spontaneous combustion. After the bulk of the residue has been collected, use moist towels to clean the porcelain tray and the inside surfaces of the exhaust hood. To reduce the hazard of spontaneous combustion occurring in the laboratory, put the moist residue from the trash container outside the building into a covered garbage can before leaving the laboratory for the day.

Standard Operating Procedure for Posting in Laboratory

A statement of laboratory procedures for posting in the laboratory was required by PRL's Safety Officer. The elements in the posted standard operating procedure prepared before conducting the tests with the more energetic oxidizers are as follows.

SAFE OPERATING PROCEDURES FOR OXIDIZER EVALUATIONS

A. Before Experiment:

1. A fire extinguisher must be located near the laboratory.
2. An eye wash and safety shower must be located near the laboratory.
3. No smoking is permitted in the laboratory.
4. No food can be stored or eaten in the laboratory.
5. Verify safe operation of exhaust hood.
6. Post a sign warning of impending combustion experiment.
7. All personnel must wear at least safety goggles or glasses, dust mask, and rubber gloves when handling fuels and safety goggles, facial HEPA filter, and rubber gloves when handling oxidizers.
8. A lab coat or apron and leather or rubber-coated cloth gloves must be worn when handling mixtures of fuel and oxidizer.

B. During Experiment:

1. Only personnel having authorized badges are permitted in the laboratory.
2. Mix fuel and oxidizer inside ventilating exhaust hood.
3. Lower hood sash to about one inch above bottom of hood.
4. Stay at least 1 meter from hood sash during ignition and combustion.

C. After Test:

1. Hood sash must be left in place for at least 5 minutes after cessation of combustion to allow

combustion gases to be exhausted from hood.

2. Goggles, HEPA filter, lab coat or apron, and leather or rubber-coated cloth gloves must be worn when cleaning debris after combustion from hood into disposal container.
3. Combustion debris must be placed outdoors to avoid possible laboratory fire.
4. In an emergency, dial the emergency help number.

Job Safety Analysis

The PRL Safety Officer required that a job safety analysis for the intended experimental effort be conducted. The analysis that was performed prior to conducting the work with the more energetic oxidizers is as follows.

JOB SAFETY ANALYSIS FOR EVALUATION OF SOLID OXIDIZER AND FUEL REACTIONS AT PRL

REQUIRED PERSONNEL PROTECTIVE EQUIPMENT: Safety goggles or glasses, dust mask, fire-resistant or cloth gloves, lab coat or apron

DETAILS OF OPERATION

HAZARD

PRECAUTIONS

1) Train operators in test procedures. Inform observers of periods when protective equipment must be worn.

1) Reagents may be toxic. Mixtures may spontaneously ignite.

1) Provide operators with on-the-job training of experimental procedure and of donning protective equipment. Do not store or eat food in the laboratory.

2) Verify that hood and equipment is operational.

2) Most mixtures and combustion products are toxic.

2) Use anemometer to measure hood entry velocity. Check condition of electrical equipment.

3) Sieve reagents in exhaust hood. Turn heater current off before mixing reagents and forming the pile of mixture in hood.

3) Skin contact or inhalation of reagents may be toxic. Rapid spontaneous combustion can occur during mixing or while forming the pile.

3) Weigh and mix reagents in hood. Operators must wear protective equipment when handling reagents and insulation, when mixing reagents, and when forming the pile.

4) Ignite conical pile of mixture of oxidizer and fuel.

4) Most combustion products are toxic.

4) Lower hood glass shield to 1" above bottom before igniting.

5) Observe combustion process and collect experimental data.

5) Combustion gases may disperse into laboratory.

5) Leave hood glass down after combustion ends for at least 5 minutes for gases to be vented. Wait until debris cools.

6) Clean up debris from experimentation.

6) Heated debris may be toxic or spontaneously ignite.

6) Wear protective equipment when cleaning hood and move debris outdoors to avoid possible laboratory fire.

*****APPENDIX D:**

Sample Data Record Form for Test Burns

1. TEST RECORD NBR: [] VIDEO: () Off () On
2. DATE: []/ []/ [] TIME: () am () pm
3. LAB TEMPERATURE & RELATIVE HUMIDITY: [] °F [] % RH
4. OPERATORS: [] & [] OBSERVER: []
5. TEST TYPE AND CATEGORY: () UN () US () Other
() Classification () Reference () Other []
6. TEST OBJECTIVE: []

7. TEST CONFIGURATION AND CONDITIONS:

Oxidant Size Range: () < 300 μ m () 150 to 300 μ m () < 150 μ m () < 90 μ m
() [< μ m] () [to μ m]

Oxidant Drying: () Oven at 65 °C () Not Dried in Oven

Reference Oxidant: () KBrO₃ () KClO₄ () (NH₄)₂S₂O₈ () Alternative KClO₃

Test Oxidant: () (NH₄)₂S₂O₈ () NH₄ClO₄ () (NH₄)₂Ce(NO₃)₆ () NH₄NO₃

() Ca(ClO)₂ () Ca(NO₃)₂·4H₂O () Mg(ClO₄)₂ () Na₂O₂ () NaNO₃

() NaClO₃ () NaClO₄·H₂O () KBrO₃ () KClO₄ () KNO₃

() KClO₃ () KNO₂ () KIO₄ () KMnO₄ () []

Fuel Size Cut: () < 1,600 μ m () []

Fuel Type: () Whatman CF-11 Cellulose () Sigma 20 Cellulose () Wood Flour

() Basswood Sawdust () Yellow Pine () []

Test Mixture Mass: () 30 grams () 20 grams () [grams]

Oxidant-with-Fuel Mixing Time: [seconds]

Oxidant-to-Fuel Mix:

Ratio (O:F): () 4:1 () 1:1 () 3:7 () 2:3 () 3:2 () [:]

Oxidant Mass: 24 g 15 g 9 g 12 g 18 g [g]

Fuel Mass: 6 g 15 g 21 g 18 g 12 g [g]

Number of Layers of Fiberfrax Used: []

Way Conical Pile Was Formed: ☐ 7.0 cm plastic funnel ☐ natural angle of repose

Nichrome Heater Wire Source: [_____]

☐ US [Open Circle] ☐ UN [Indented Circle]

Wire Length [_____ cm] AWG [_____] Resistance [_____ Ω]

Current [_____ Amps] Power [_____ Watts]

Optical Pyrometric Temperature of Bare Wire: [_____ $^{\circ}\text{C}$]

Heating Mode: ☐ left on ☐ turned off after [_____ seconds]

Location of Heating Wire: ☐ At Base of Cone ☐ At Middle of Cone

☐ Near Top of Cone

8. OBSERVATIONS:

Start of Smoking [_____ sec] [NONE AFTER _____ minutes]

Start of Intense Smoking [_____ sec] [NONE AFTER _____ minutes]

Start of Open Flaming [_____ sec] [NONE AFTER _____ minutes]

Start of Intense Open Flaming [_____ sec]

End of Open Flaming of Main Pile [_____ sec] UN Burn Time [_____] seconds

End of Smoking of Main Pile [_____ sec]

End of Outlier Flaming [_____ sec] US Burn Time [_____] seconds

Last Glow of Main pile [_____ sec] [Reported as = (END - START)]

Last Glow of Outlier [_____ sec]

Residue ☐ Considerable Mass ☐ Small Mass Estimated Mass [_____ g]

9. TEST OUTCOME AND ADDITIONAL COMMENTS:

*****APPENDIX E:**

Graphs of Burning Times versus Mass Ratios

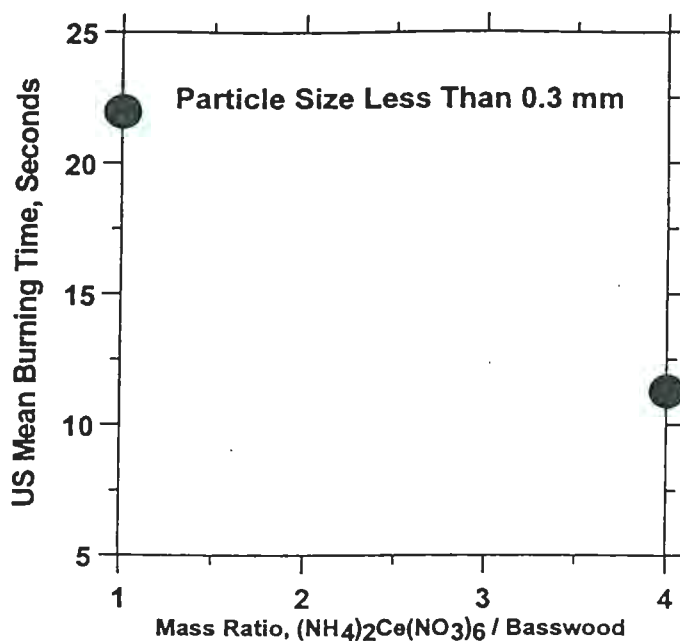


Figure E-1. US mean burning time versus $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ -basswood mass ratio for oxidizer with particle size range less than 0.3 mm

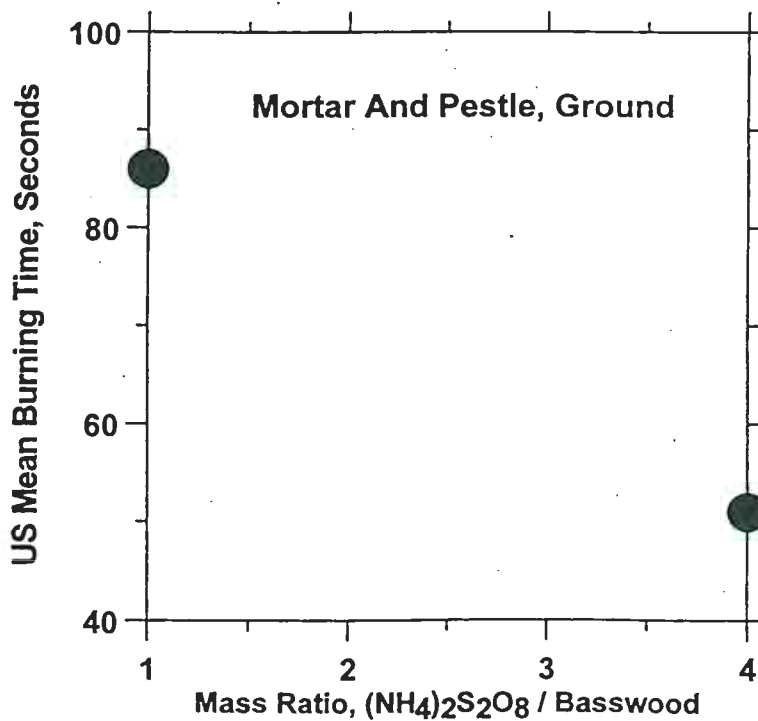


Figure E-2. US mean burning time versus $(\text{NH}_4)_2\text{S}_2\text{O}_8$ -basswood mass ratio for ground oxidizer

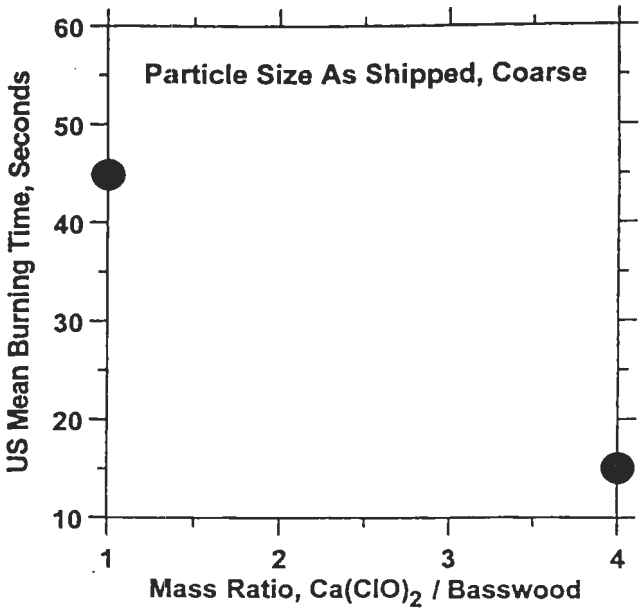


Figure E-3. US mean burning time versus $\text{Ca}(\text{ClO})_2$ -basswood mass ratio for coarse oxidizer

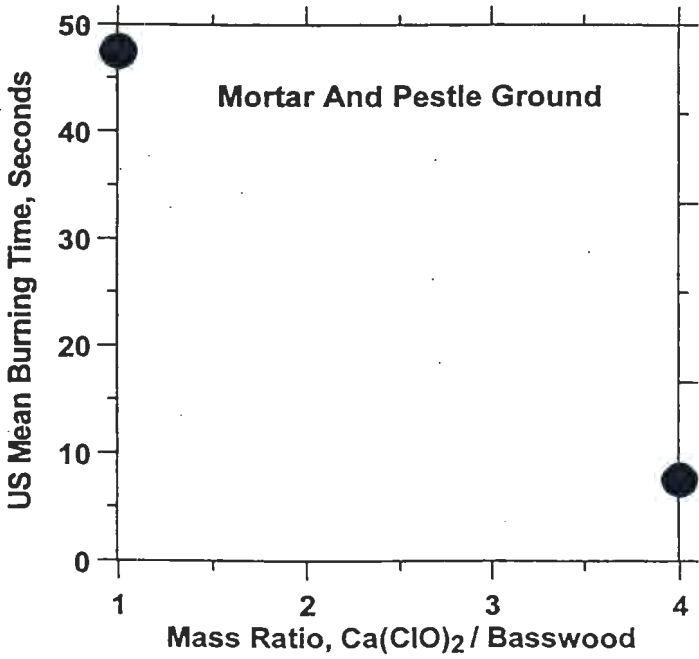


Figure E-4. US mean burning time versus $\text{Ca}(\text{ClO})_2$ -basswood mass ratio for ground oxidizer

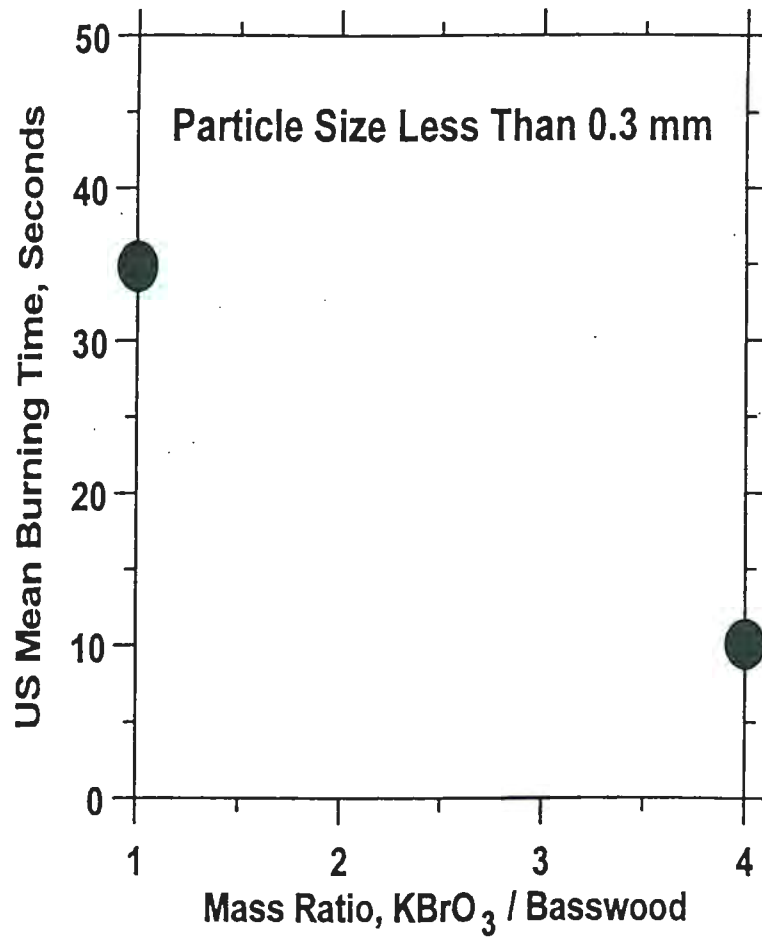


Figure E-5. US mean burning time versus KBrO_3 -basswood mass ratio for oxidizer with particle size range less than 0.3 mm

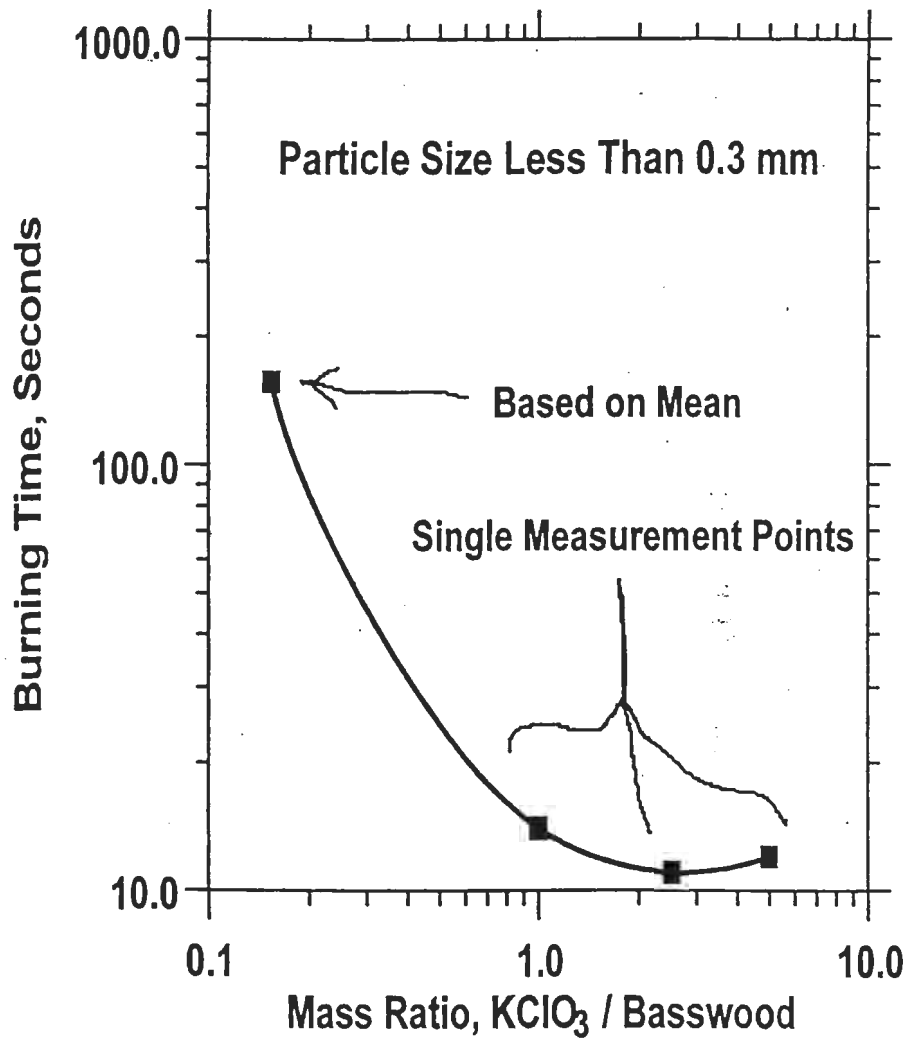


Figure E-6. US mean burning time versus KClO_3 -basswood mass ratio for oxidizer with particle size range less than 0.3 mm

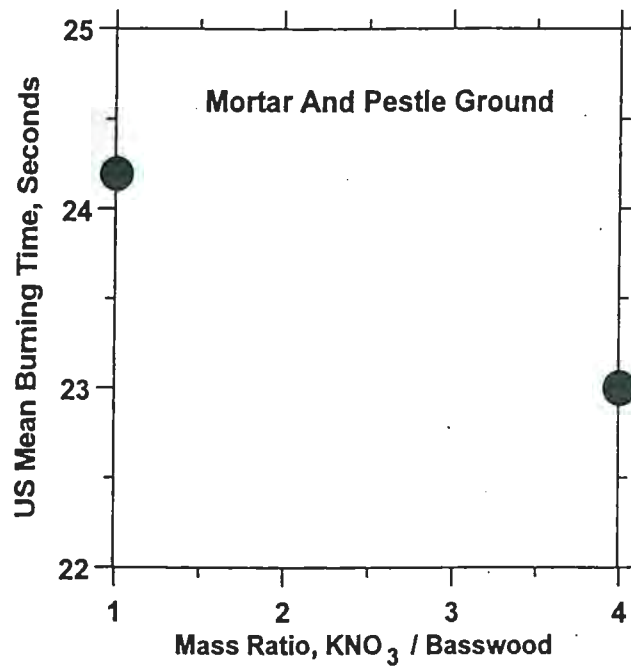


Figure E-7: US mean burning time versus KNO_3 -basswood mass ratio for ground oxidizer

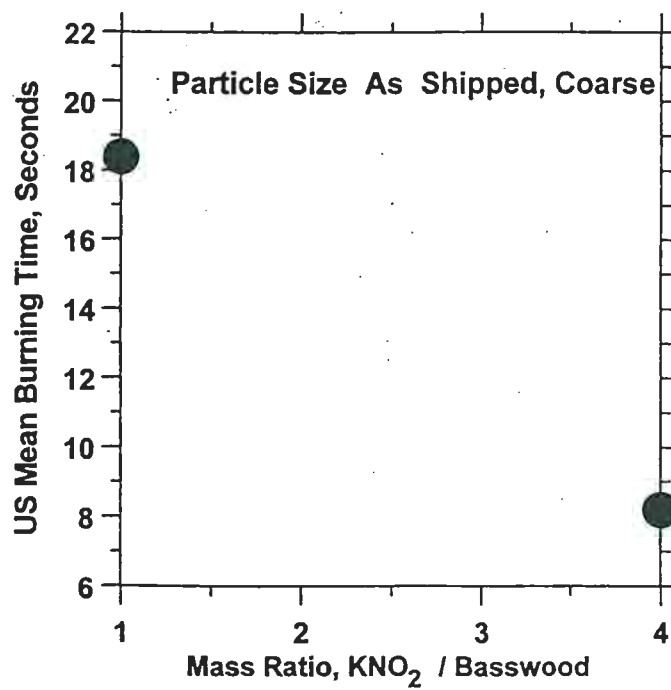


Figure E-8. US mean burning time versus KNO_2 -basswood mass ratio for coarse oxidizer

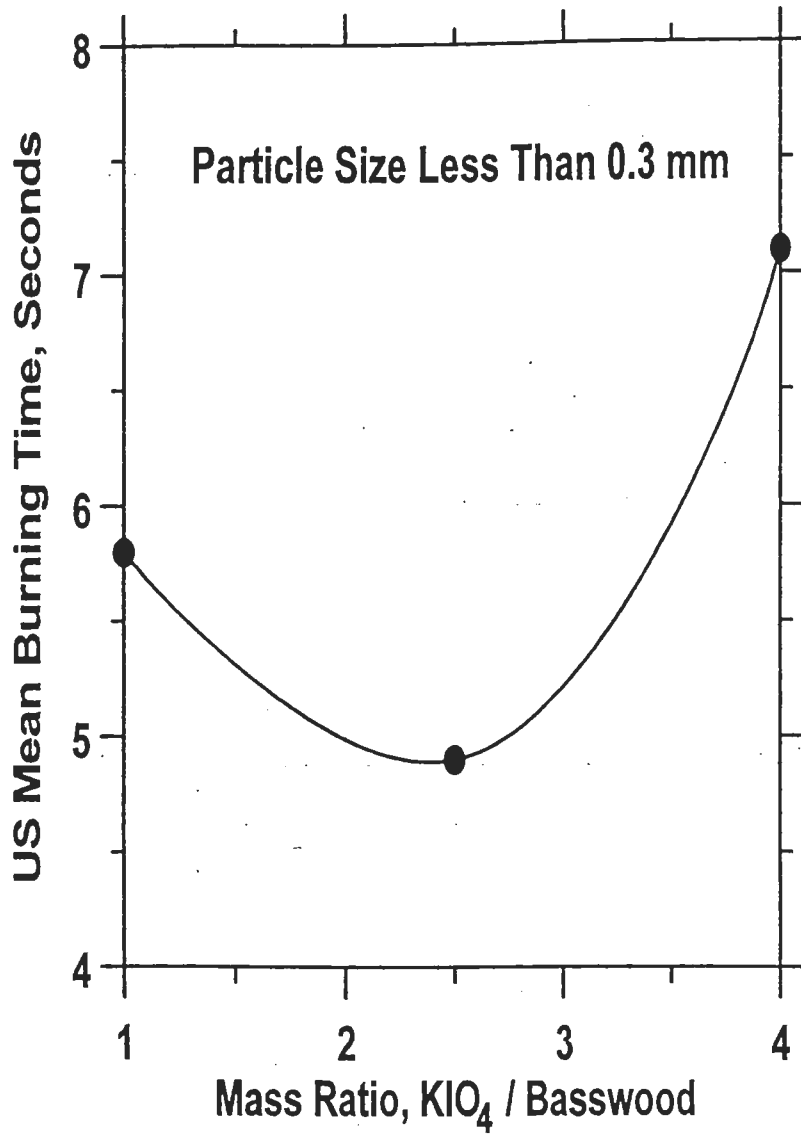


Figure E-9. US mean burning time versus KIO_4 -basswood mass ratio for oxidizer with particle size range less than 0.3 mm

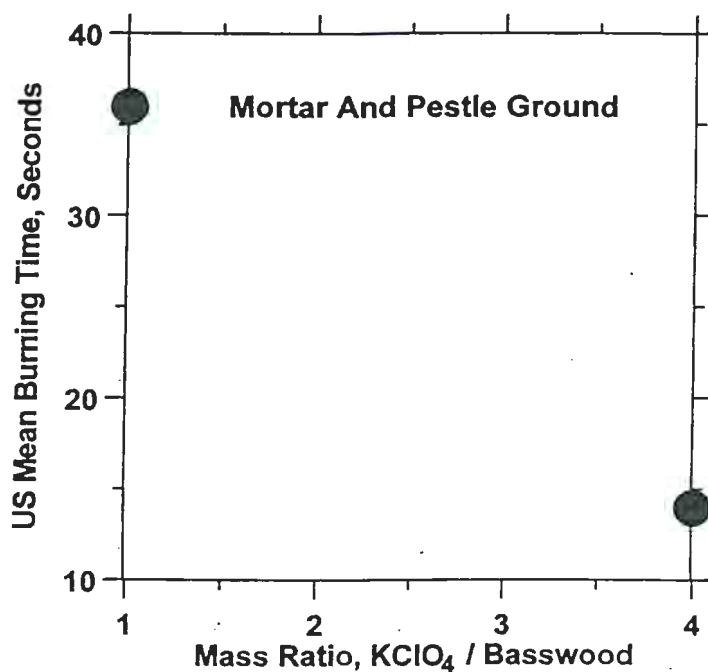


Figure E-10. US mean burning time versus KClO_4 -basswood mass ratio for ground oxidizer

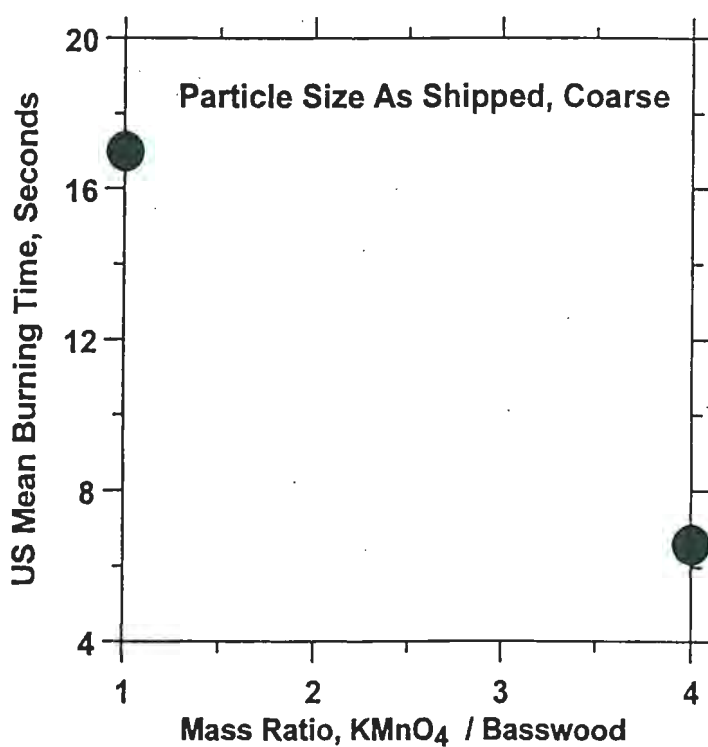


Figure E-11. US mean burning time versus KMnO_4 -basswood mass ratio for coarse oxidizer

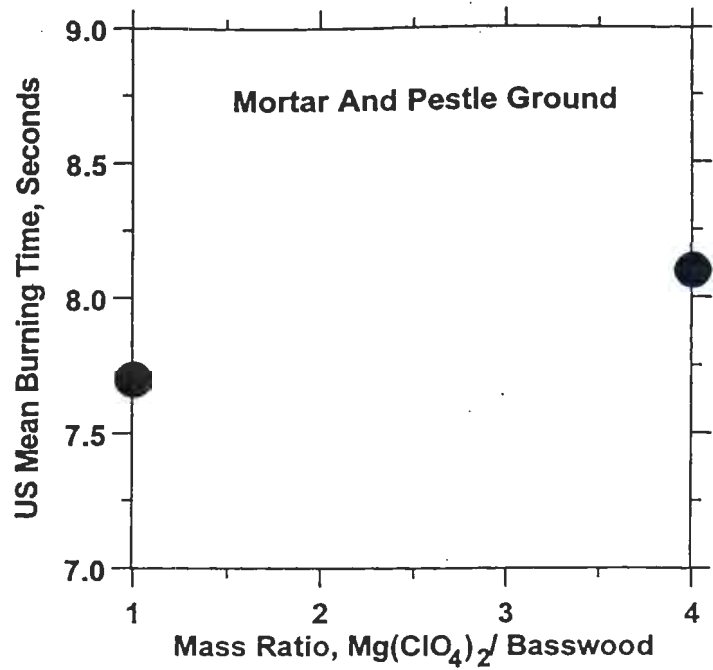


Figure E-12. US mean burning time versus $\text{Mg}(\text{ClO}_4)_2$ -basswood mass ratio for coarse oxidizer

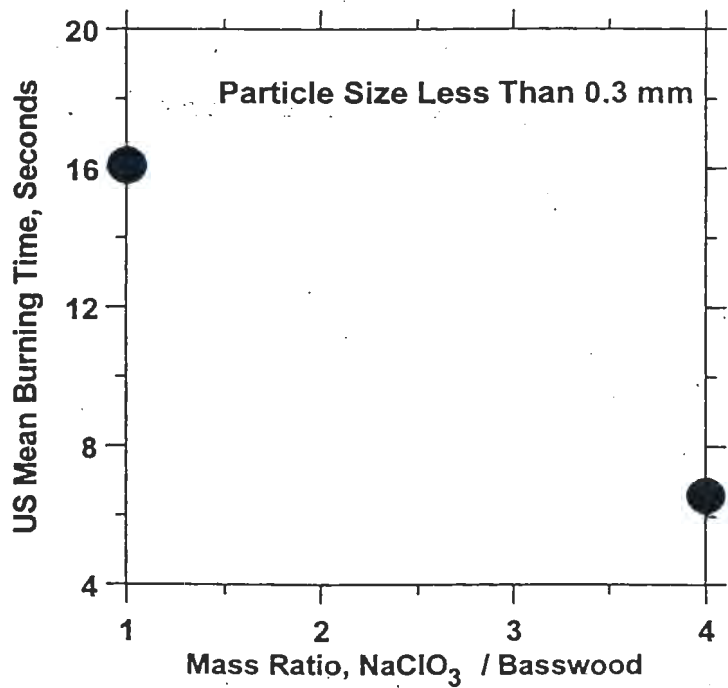


Figure E-13. US mean burning time versus NaClO_3 -basswood mass ratio for oxidizer with particle size range less than 0.3 mm

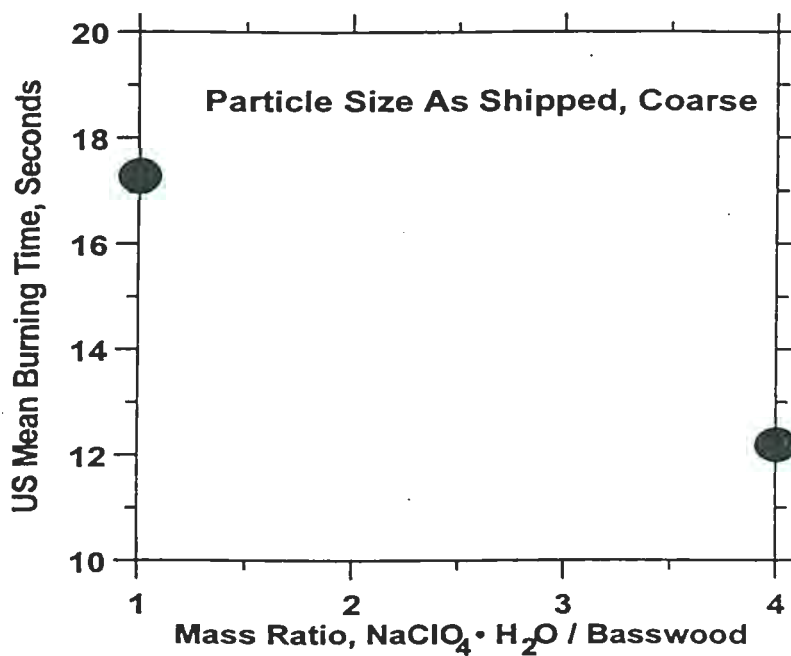


Figure E-14. US mean burning time versus $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ -basswood mass ratio for coarse oxidizer

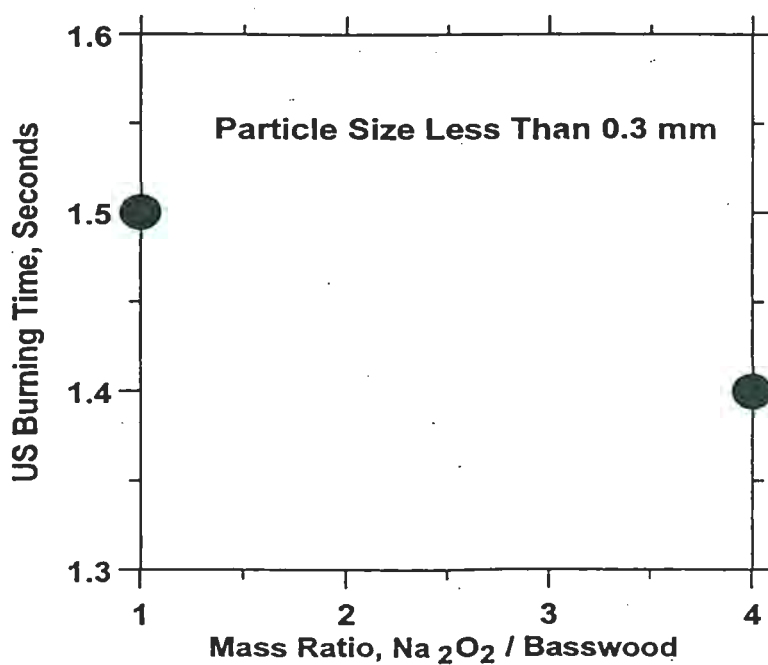


Figure E-15. US mean burning time versus Na_2O_2 -basswood mass ratio for oxidizer with particle size range less than 0.3 mm

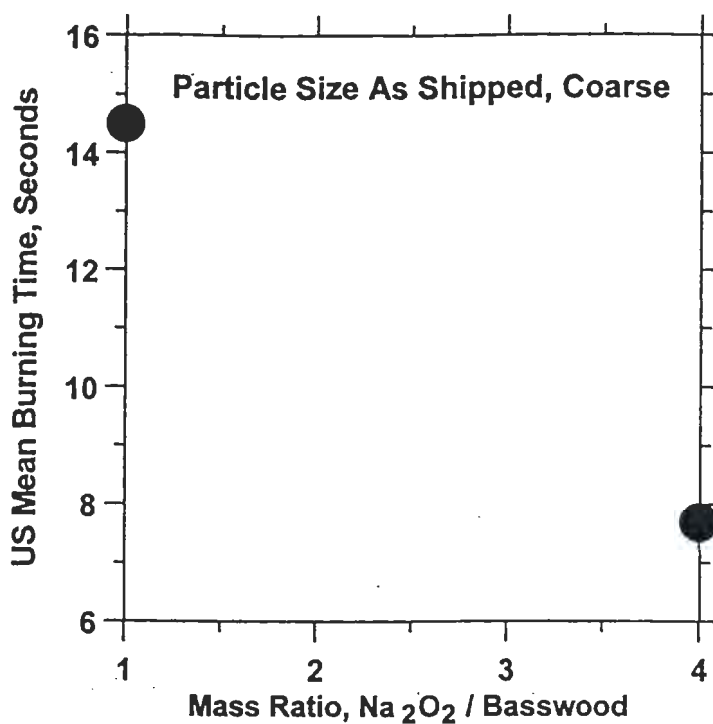


Figure E-16. US mean burning time versus Na_2O_2 -basswood mass ratio for coarse oxidizer

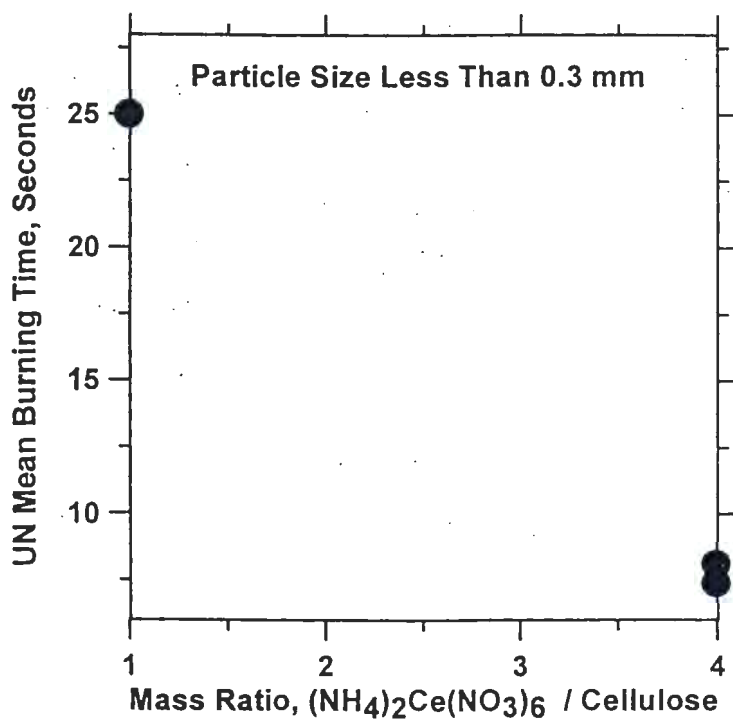


Figure E-17. UN mean burning time versus $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ -cellulose mass ratio for oxidizer with particle size less than 0.3 mm

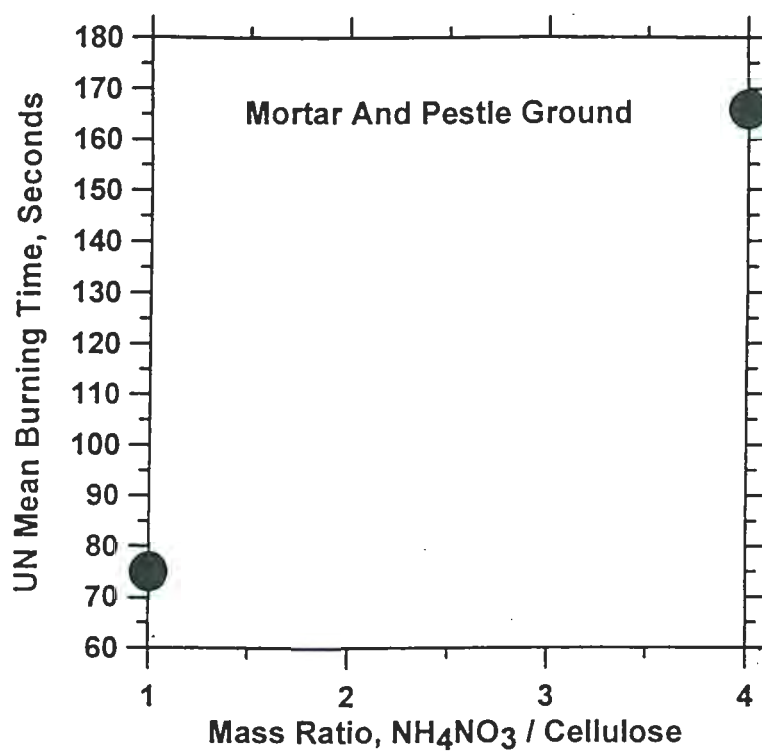


Figure E-18. UN mean burning time versus NH_4NO_3 -cellulose mass ratio for ground oxidizer

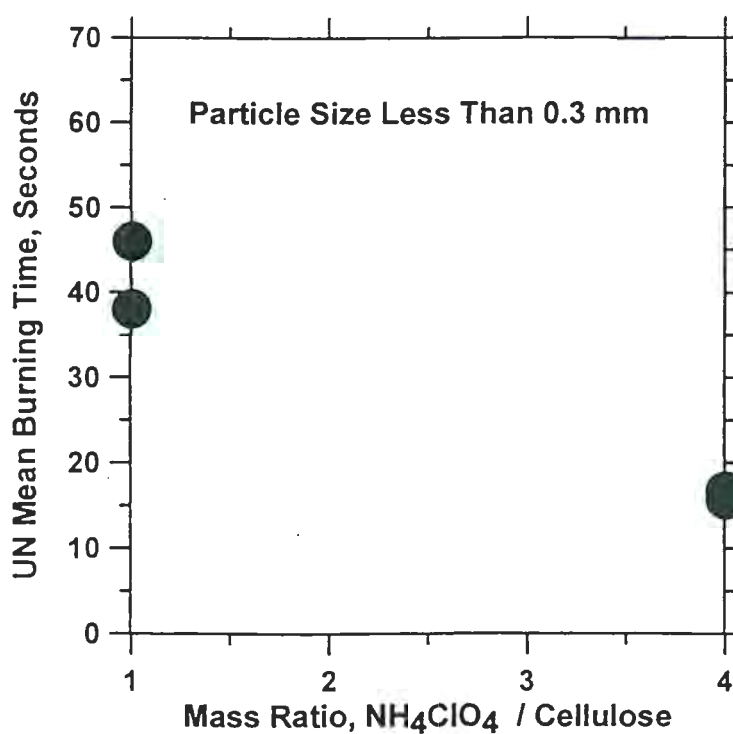


Figure E-19. UN mean burning time versus NH_4ClO_4 -cellulose mass ratio for oxidizer with particle size range less than 0.3 mm

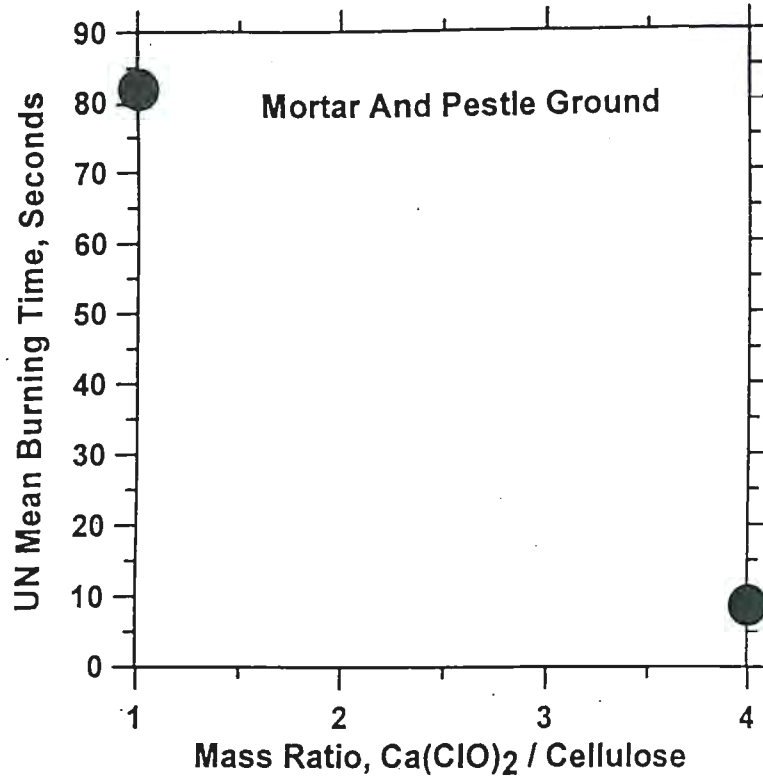


Figure E-20. UN mean burning time versus $\text{Ca}(\text{ClO})_2$ -cellulose for ground oxidizer

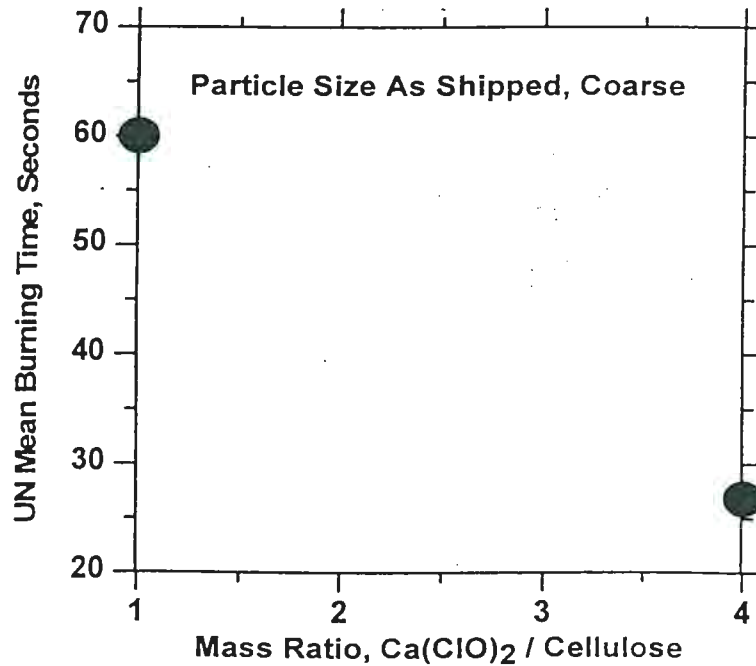


Figure E-21. UN mean burning time versus $\text{Ca}(\text{ClO})_2$ -cellulose mass ratio for coarse oxidizer

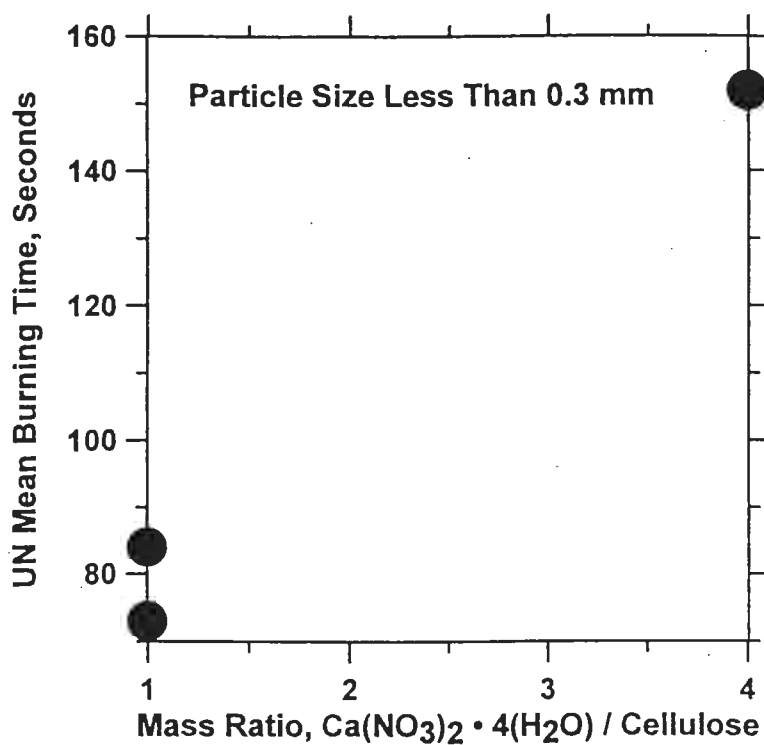


Figure E-22. UN mean burning time versus $\text{Ca}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$ -cellulose mass ratio for oxidizer with particle size range less than 0.3 mm

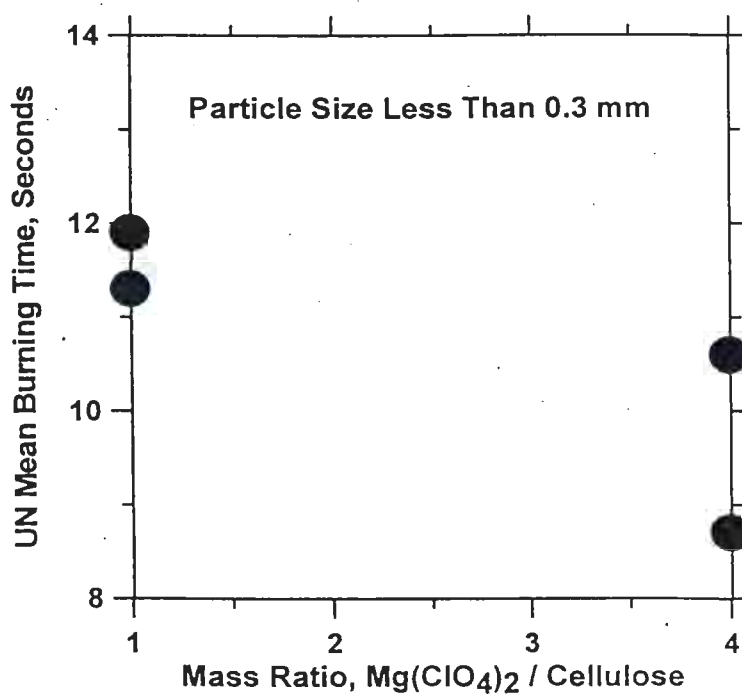


Figure E-23. UN mean burning time versus $\text{Mg}(\text{ClO}_4)_2$ -cellulose mass ratio for oxidizer with particle size range less than 0.3 mm

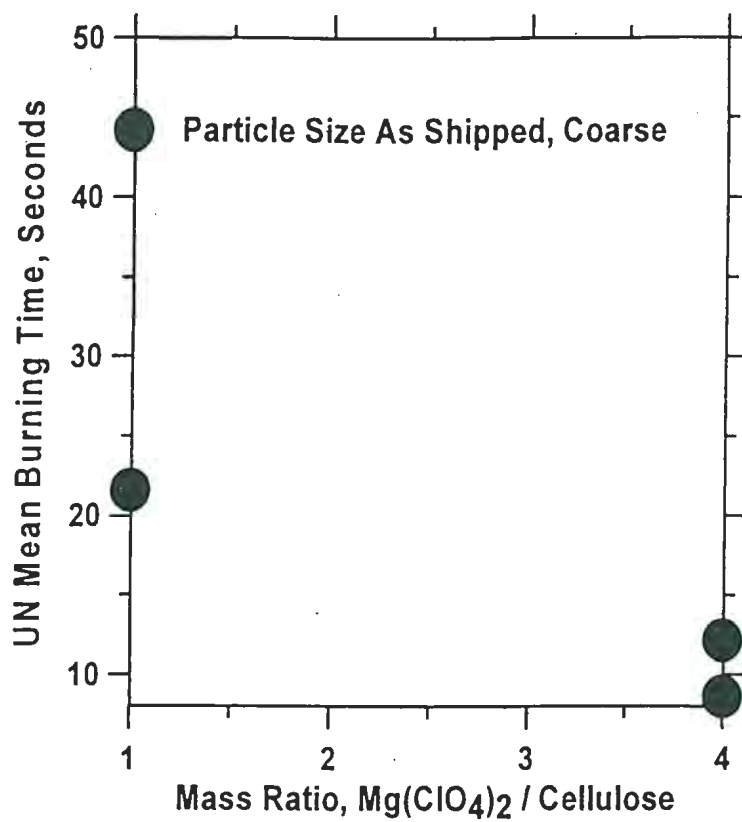


Figure E-24. UN mean burning time versus $\text{Mg}(\text{ClO}_4)_2$ -cellulose mass ratio for coarse oxidizer

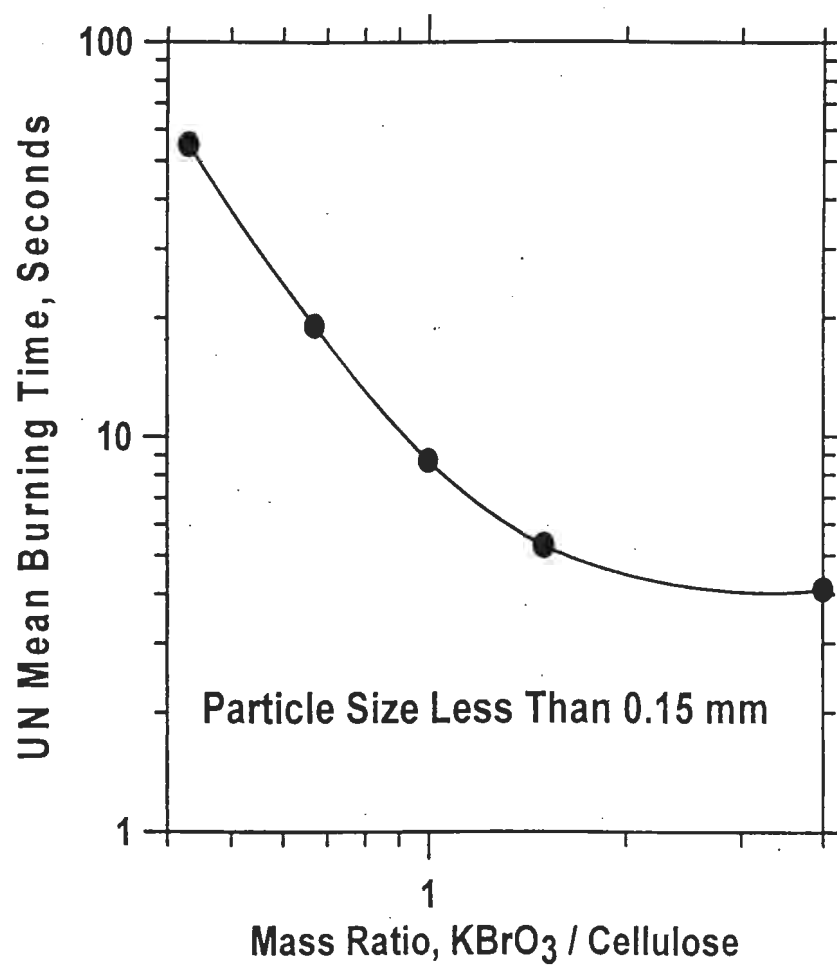


Figure E-25. UN mean burning time versus KBrO_3 -cellulose mass ratio for oxidizer with particle size range less than 0.15 mm

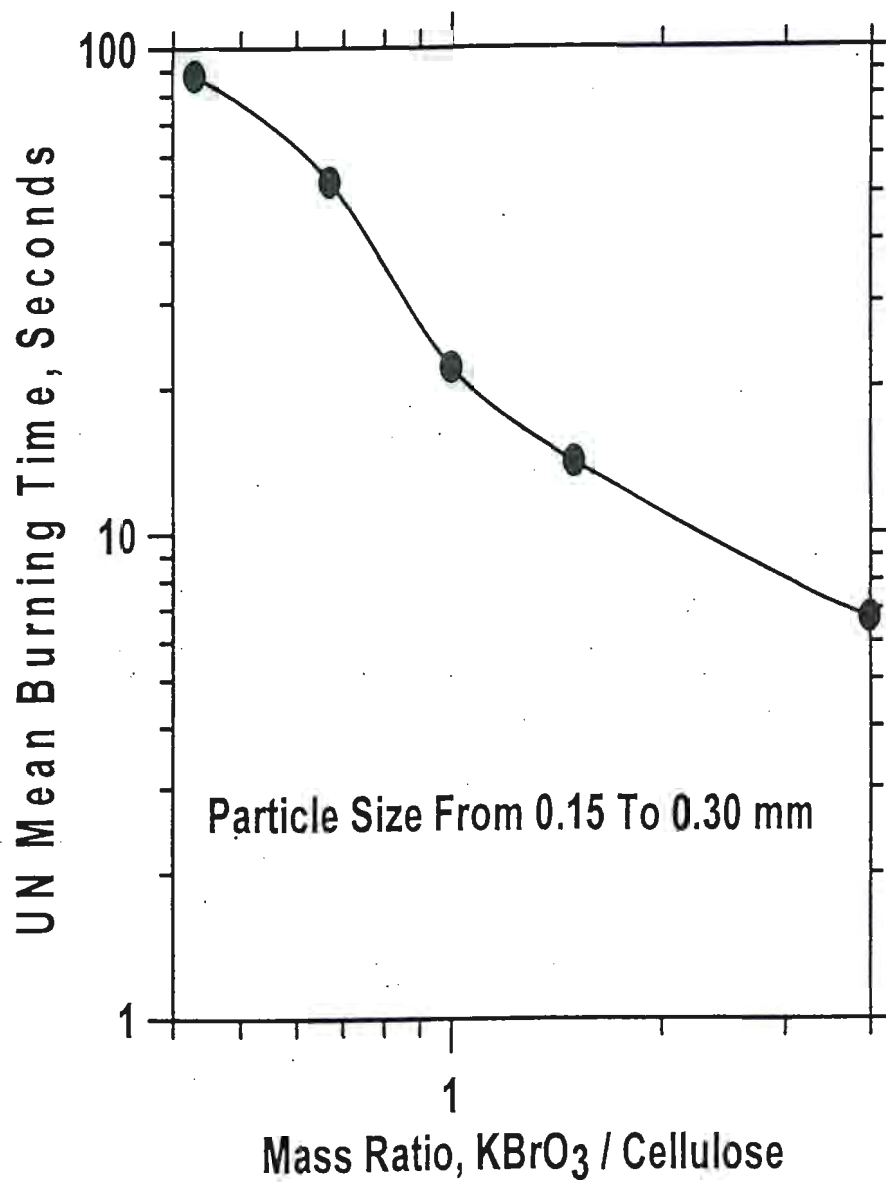


Figure E-26. UN mean burning time versus KBrO_3 -cellulose mass ratio for oxidizer with particle size range from 0.15 to 0.3 mm

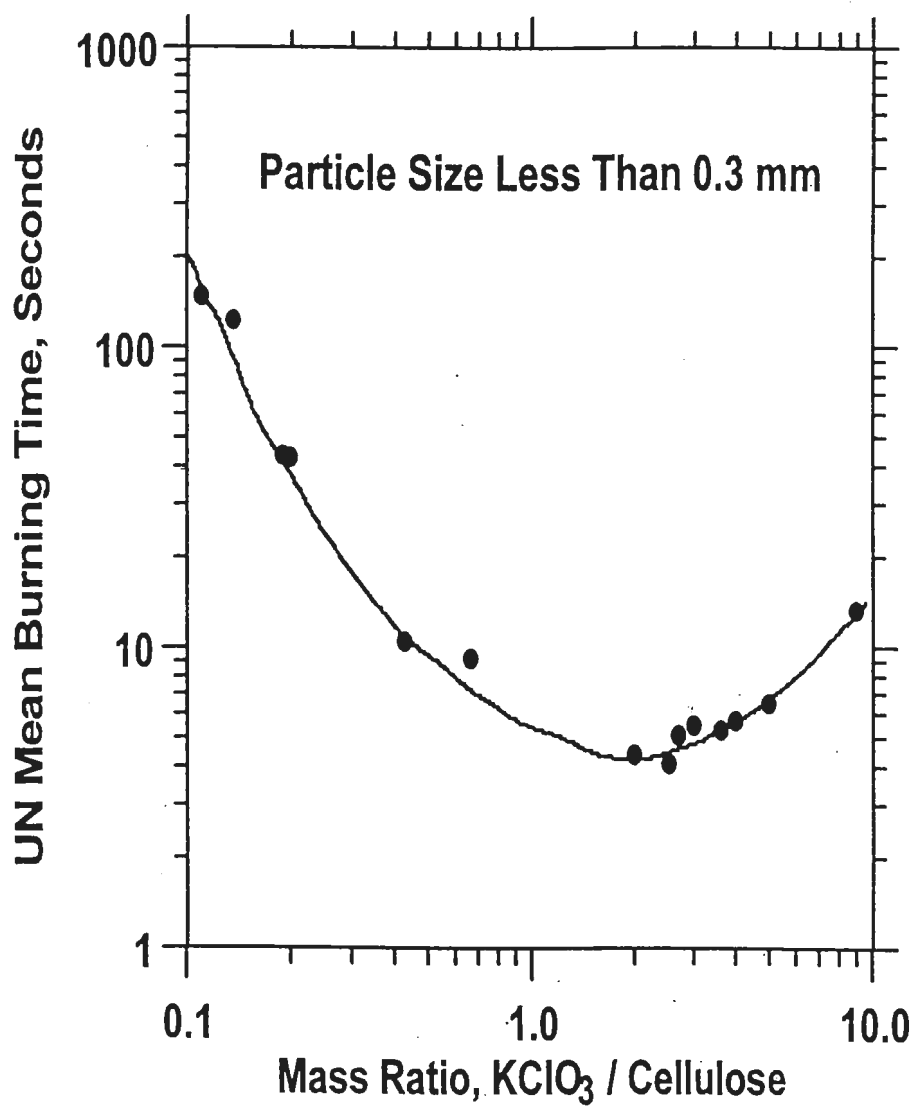


Figure E-27. UN mean burning time versus KClO_3 - fuel mass ratio for oxidizer with particle size range less than 0.3 mm

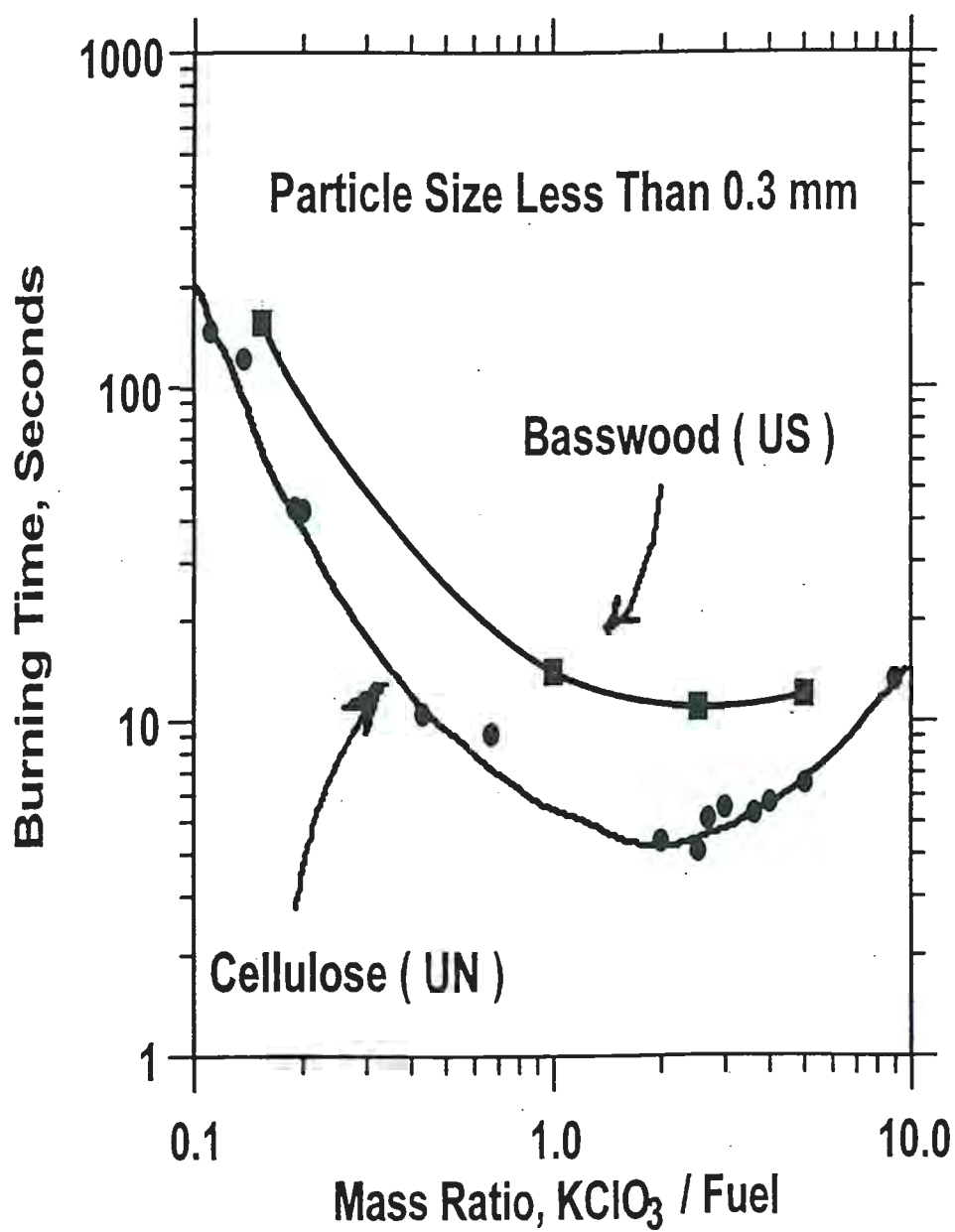


Figure E-28. UN & US burning times versus KClO_3 - fuel mass ratio for oxidizer with particle size range less than 0.3 mm

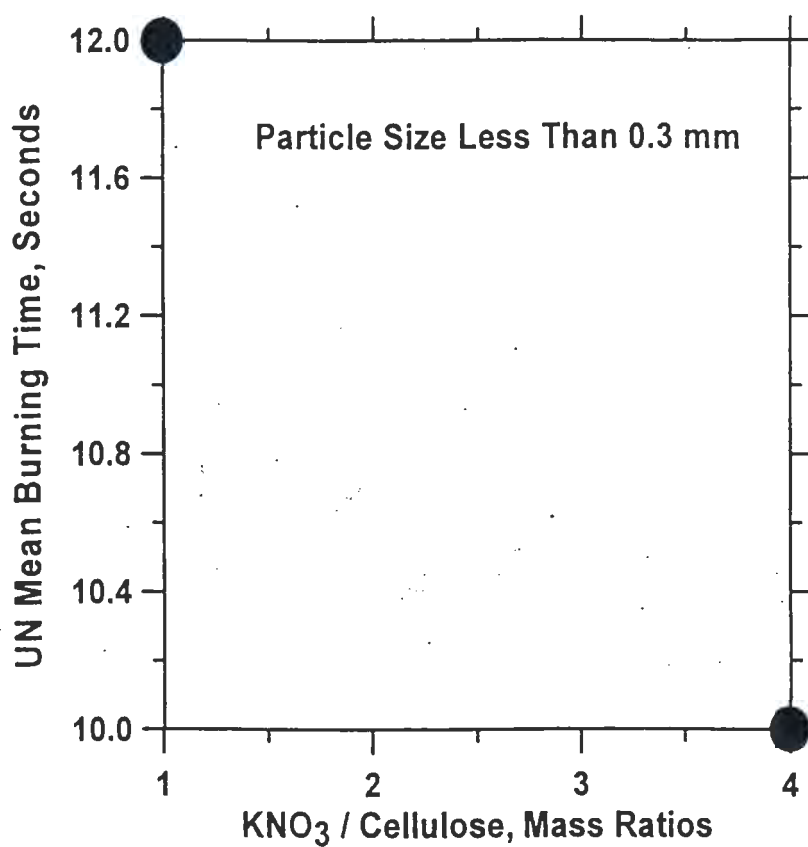


Figure E-29. UN mean burning time versus KNO₃-cellulose mass ratio for oxidizer with particle size range less than 0.3 mm

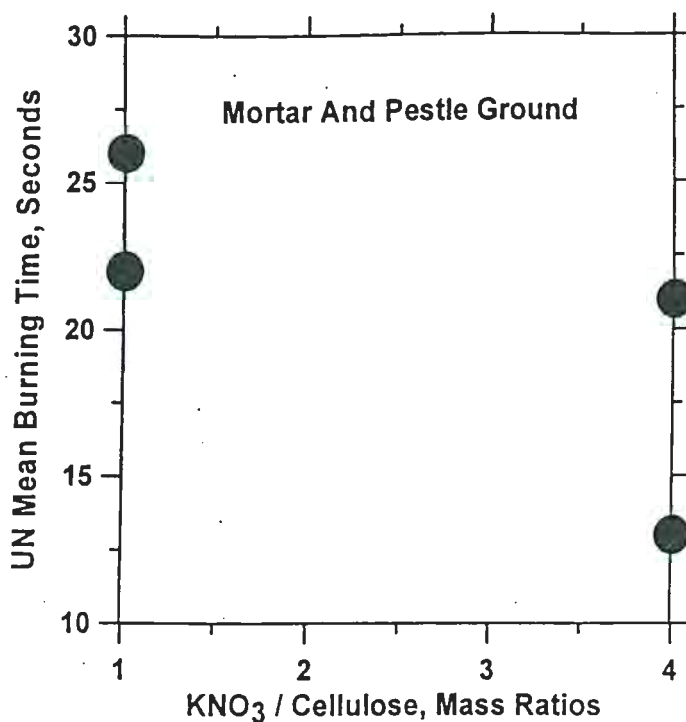


Figure E-30. UN mean burning time versus KNO₃-cellulose mass ratio for ground oxidizer

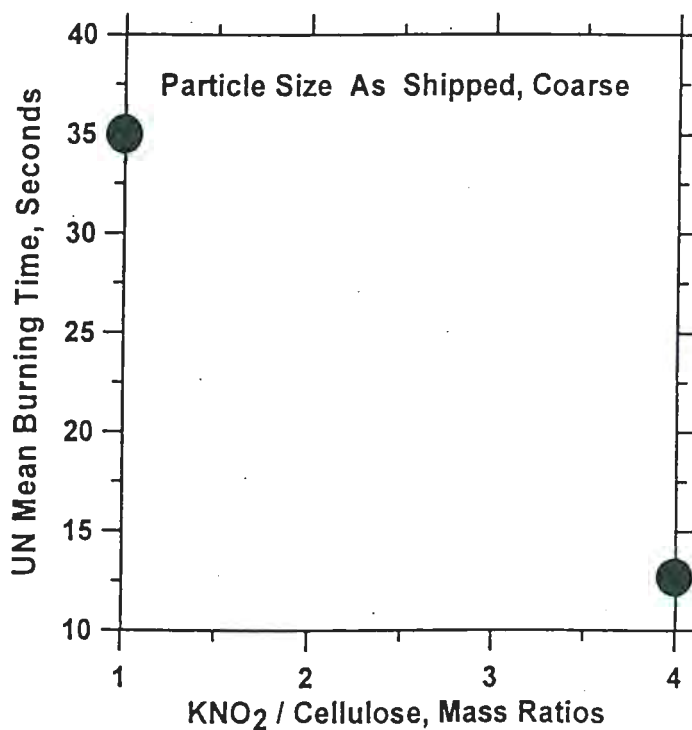


Figure E-31. UN mean burning time versus KNO₂-cellulose mass ratio for coarse oxidizer

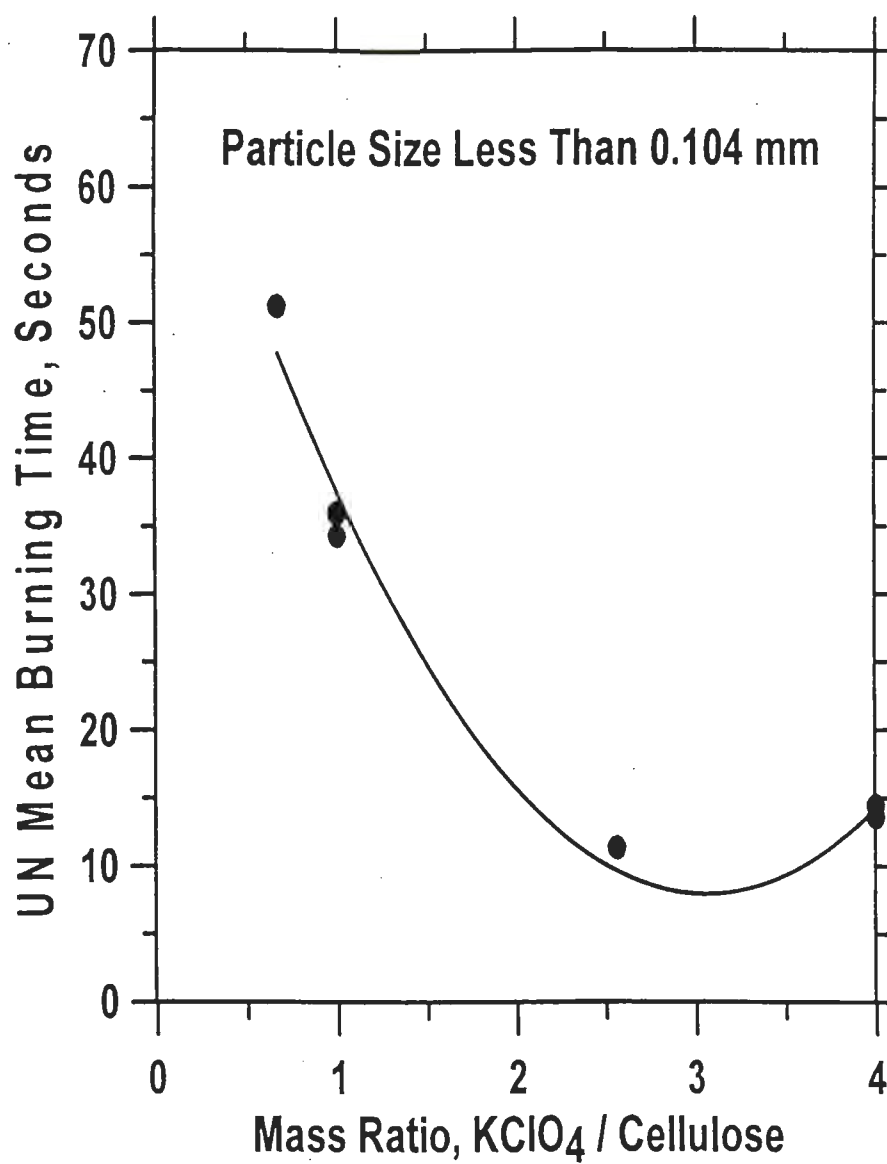


Figure E-32. UN mean burning time versus KClO_4 -cellulose mass ratio for oxidizer with particle size range less than 0.104 mm

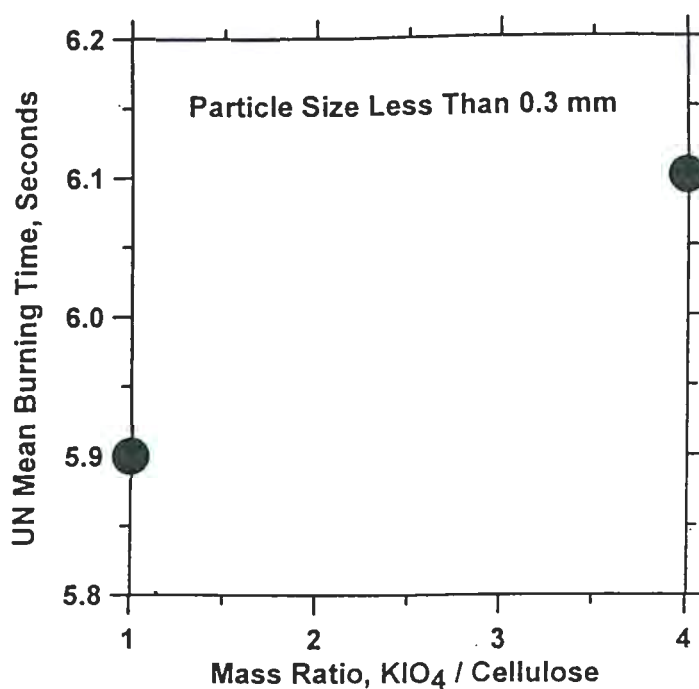


Figure E-33. UN mean burning time versus KIO₄-cellulose mass ratio for oxidizer with particle size range less than 0.3 mm

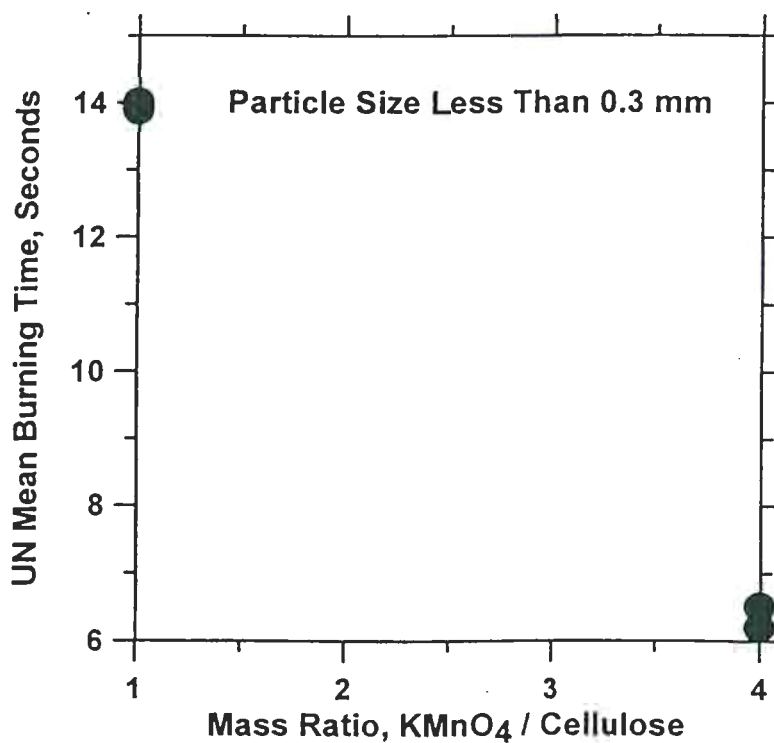


Figure E-34. UN mean burning time versus KMnO₄-cellulose mass ratio for oxidizer with particle size range less than 0.3 mm

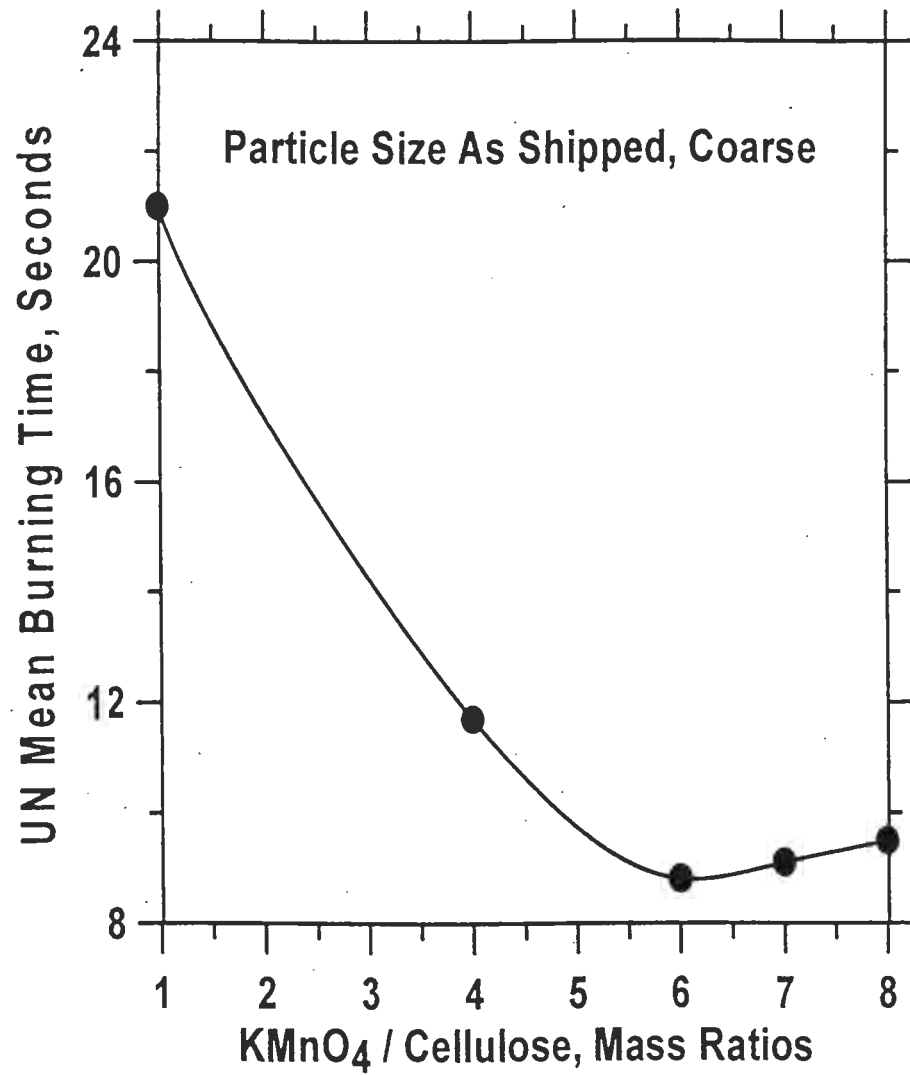


Figure E-35. UN mean burning time versus KMnO_4 -cellulose mass ratio for coarse oxidizer

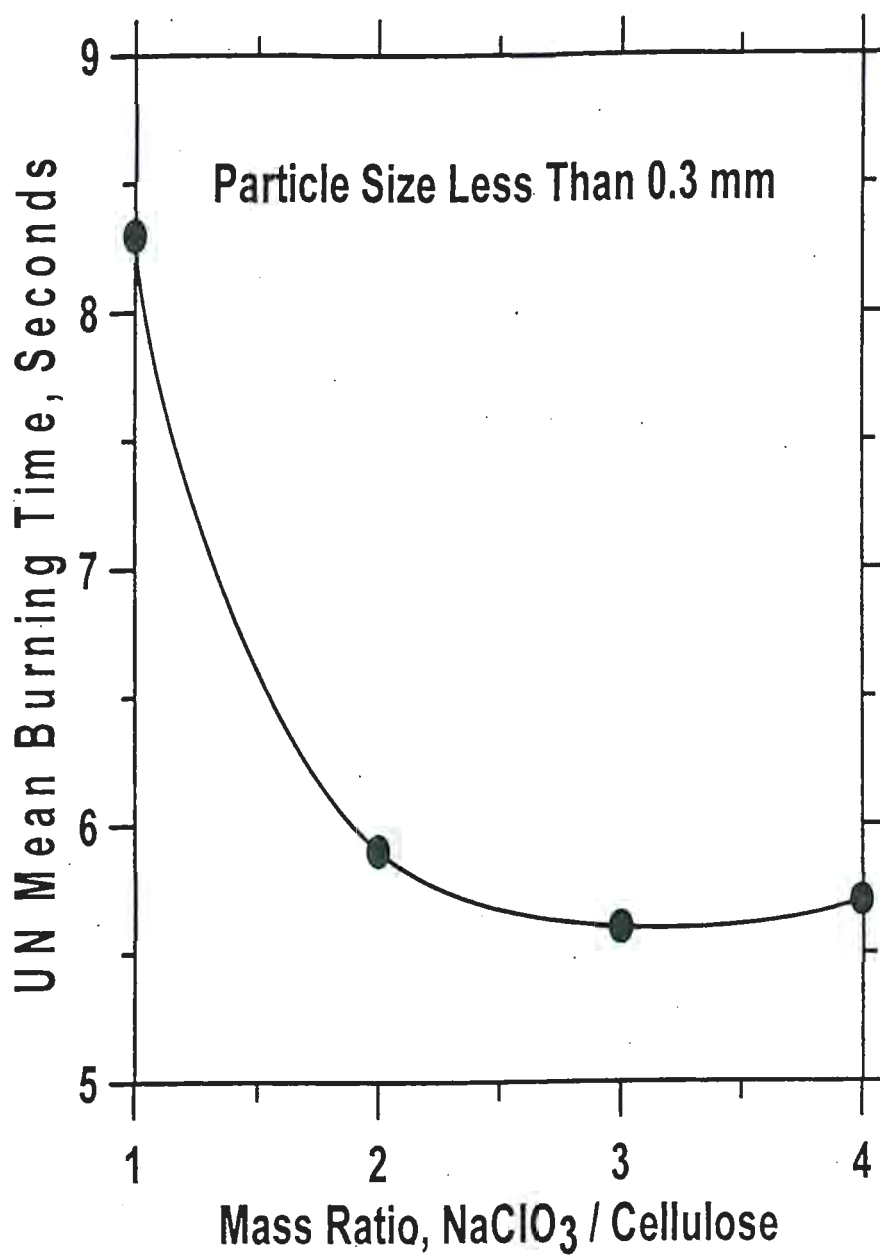


Figure E-36. UN mean burning time versus NaClO_3 -cellulose mass ratio for oxidizer with particle size range less than 0.3 mm

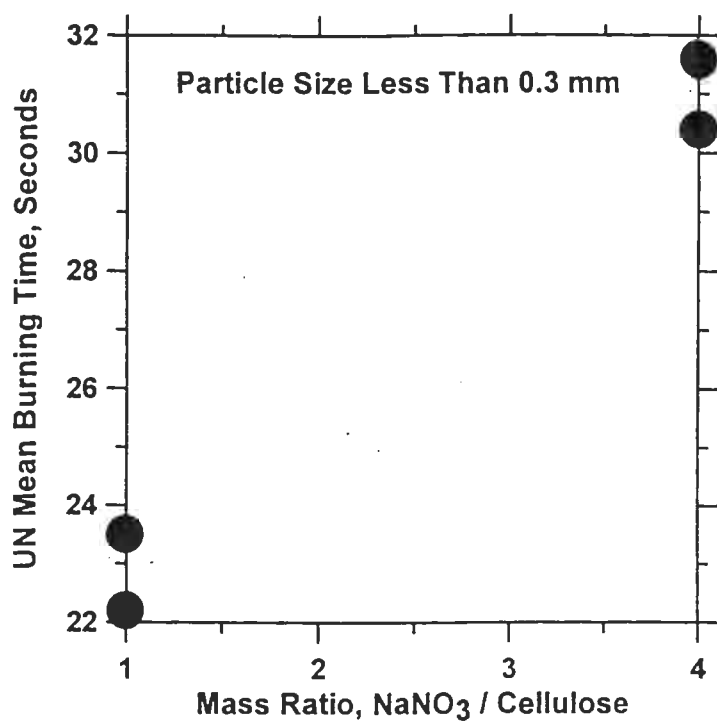


Figure E-37. UN mean burning time versus NaNO_3 -cellulose mass ratio for oxidizer with particle size range less than 0.3 mm

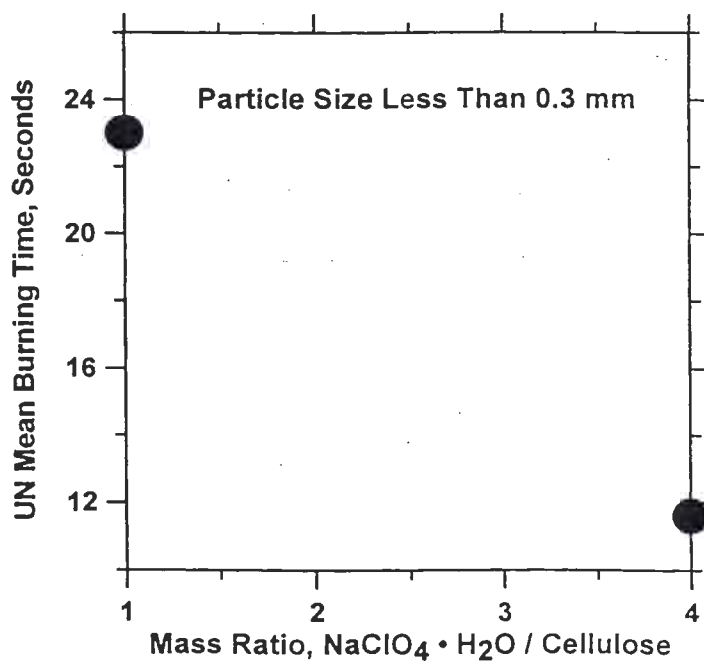


Figure E-38. UN mean burning time versus $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ -cellulose mass ratio for oxidizer with particle size range less than 0.3 mm

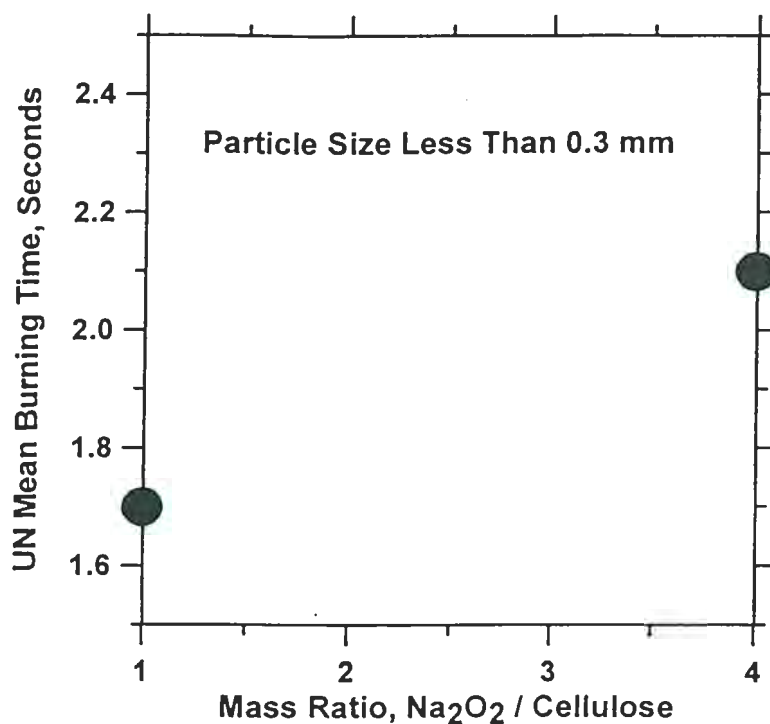


Figure E-39. UN mean burning time versus Na_2O_2 -cellulose mass ratio for oxidizer with particle size range less than 0.3 mm

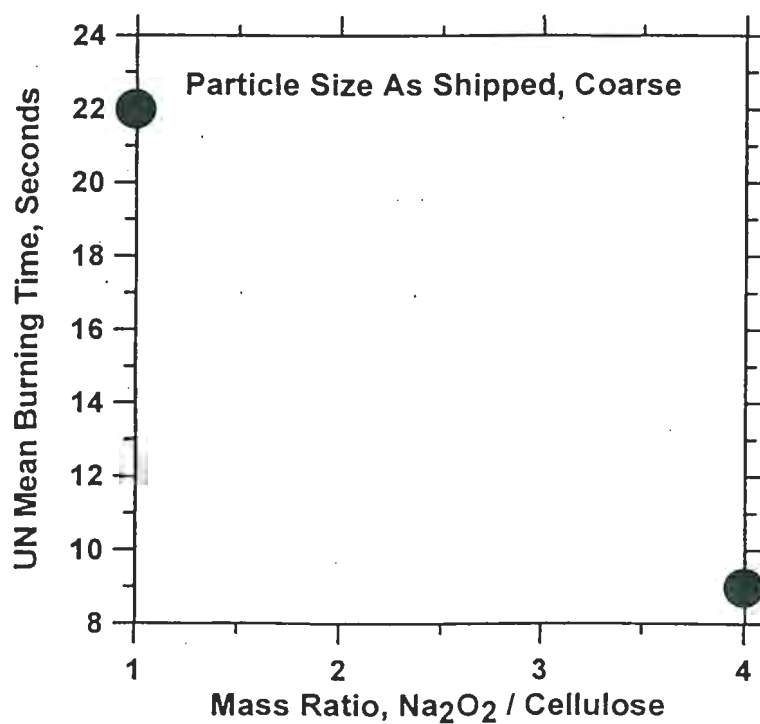


Figure E-40. UN mean burning time versus Na_2O_2 -cellulose mass ratio for coarse oxidizer

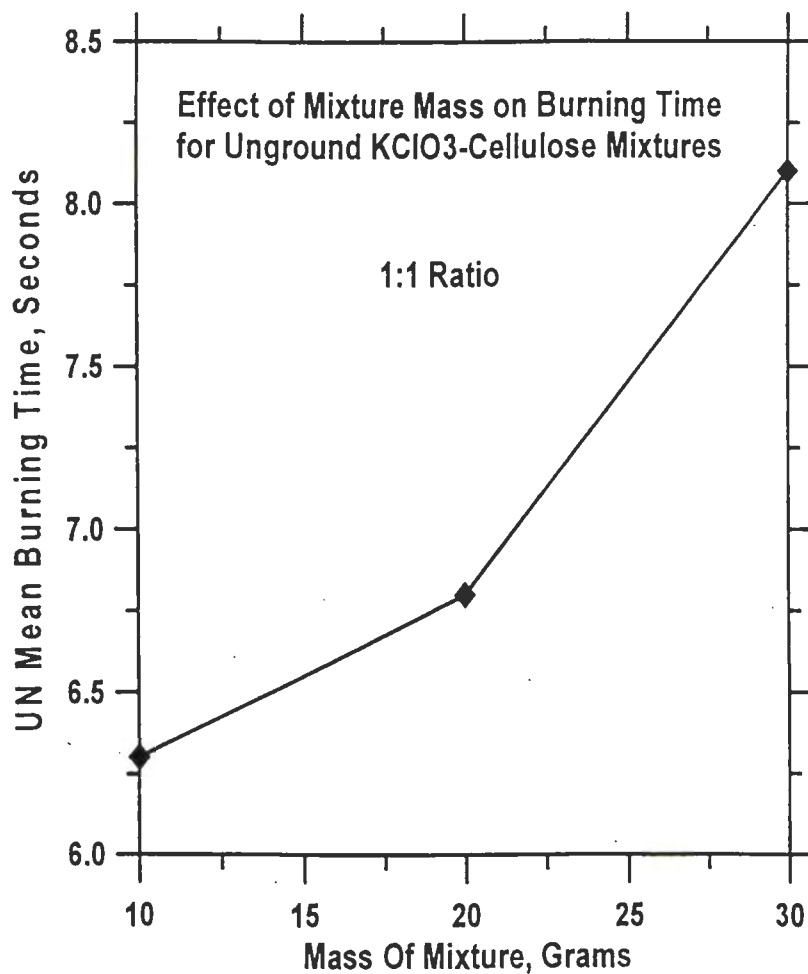


Figure E-41. Effect of mixture mass on UN burning time for unground KClO₃-cellulose mixtures

*****APPENDIX F:****Tables of UN and US Burning Times**

Table F-1.--Reference Oxidizers for UN and US procedures

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burn Time, Seconds (s)
150	KBrO ₃	Cellulose	3/7	80
156	"	"	3/7	78
158	"	"	3/7	97
183	"	"	3/7	96
184	"	"	3/7	86
185	"	"	3/7	90
For the above test set: N = 6, av = 88 s, and SD = 8 s. Particle size range for above test set is 0.15 mm to 0.3 mm.				
224	KBrO ₃	Cellulose	3/7	55
225	"	"	3/7	50
226	"	"	3/7	60
227	"	"	3/7	60
228	"	"	3/7	50
For the above test set: N = 3, av = 55 s, and SD = 5 s. Particle size range for above test set is 0 mm to 0.15 mm.				
151	KBrO ₃	Cellulose	2/3	47
155	"	"	2/3	67
157	"	"	2/3	60
186	"	"	2/3	43
187	"	"	2/3	49
For the above test set: N = 5, av = 53 s, and SD = 10 s. Particle size range for above test set is 0.15 mm to 0.3 mm.				
218	KBrO ₃	Cellulose	2/3	21.0
219	"	"	2/3	19.8
220	"	"	2/3	19.5
221	"	"	2/3	20.0
222	"	"	2/3	19.5
223	"	"	2/3	14.9

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burn Time, Seconds (s)
For the above test set: N = 6, av = 19.1 s, and SD = 2.1 s. Particle size range for above test set is 0 mm to 0.15 mm.				
152	KBrO ₃	Cellulose	3/2	15.6
154	"	"	3/2	13.4
178	"	"	3/2	15.5
179	"	"	3/2	14.3
180	"	"	3/2	14.6
188	"	"	3/2	13.2
189	"	"	3/2	12.4
For the above test set: N = 7, av = 14.1 s, and SD = 1.2 s. Particle size range for above test set is 0.15 mm to 0.3 mm.				
212	KBrO ₃	Cellulose	3/2	4.0
214	"	"	3/2	5.5
215	"	"	3/2	6.3
216	"	"	3/2	5.3
217	"	"	3/2	5.2
For the above test set: N = 5, av = 5.3 s, and SD = 0.8 s. Particle size range for above test set is 0 mm to 0.15 mm.				
170	(NH ₄) ₂ S ₂ O ₈	Basswood	1/1	85.0
171	"	"	1/1	88.0
174	"	"	1/1	85.0
For the above test set: N = 3, av = 86.0 s, and SD = 1.7 s. SCO was ground using a mortar and pestle. The power was turned off within about 25 seconds once intense smoking occurred.				
754	(NH ₄) ₂ S ₂ O ₈	Basswood	1/1	>180
755	"	"	1/1	230
756	"	"	1/1	200

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burn Time, Seconds (s)
SCO particle size was less than 0.3 mm. The power was turned off after about 120 seconds of heating. No open flaming occurred in Test 754 and smoking commenced after 6 seconds. Open flaming occurred in Test 755 from 14 seconds until 120 seconds, and smoking started at 6 seconds and ceased at 230 seconds. In Test 756 open flaming took place between 16 seconds and 60 seconds, and smoking commenced at 5 seconds and ceased at 200 seconds. The reaction which was initiated from within ceased before reaching most of the surface, leaving considerable fuel unburned.				
757	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	Cellulose	4/1	200
758	"	"	4/1	>180
SCO particle size was less than 0.3 mm. The power was kept on. In Test 757 smoking commenced after 3 seconds and ceased at 200 seconds. In Test 757, observation at the end of smoking revealed a liquid had formed on the pile; most likely it was water. In Test 758 smoking commenced after 7 seconds. During the combustion process ammonia, carbon dioxide, water, and sulfur dioxide were produced. Also during combustion, a thin black carbonaceous shell formed on the surface of the pile, and the pile swelled to several times its original volume.				
759	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	Cellulose	1/1	>180
SCO particle size was less than 0.3 mm. The power was kept on. In Test 759 smoking commenced after 4 seconds.				
715	KBrO_3	Basswood	1/1	30
716	"	"	1/1	29
717	"	"	1/1	39
718	"	"	1/1	55.5
719	"	"	1/1	25.5
720	"	"	1/1	50.0
721	"	"	1/1	69.0 Outlier
722	"	"	1/1	84.0 Outlier
723	"	"	1/1	37.0
724	"	"	1/1	51.0
For the above test set: N = 10 av = 47 s and SD = 18.8 s Particle size range for above test set is 0 mm to 0.3 mm Rejecting # 721 and 722 as outliers gives for N = 8, av = 39.6 s and SD = 11.3 s				
725	KBrO_3	Basswood	4/1	17
726	"	"	4/1	13

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burn Time, Seconds (s)
727	"	"	4/1	13.5
728	"	"	4/1	12
729	"	"	4/1	17.5
For the above test set: N = 5	av = 14 s and SD = 2.4 s	Particle size range for above test set is 0 mm to 0.3 mm		
161	KClO ₄	Basswood	1/1	36
162	"	"	1/1	36
163	"	"	1/1	37
For the above test set: N = 3, av = 36 s, and SD = 1 s. SCO was ground using a mortar and pestle.				
164	KClO ₄	Basswood	4/1	14.0
165	"	"	4/1	14.0
166	"	"	4/1	14.0
For the above test set: N = 3, av = 14.0 s, and SD = 0.0 s. SCO was ground using a mortar and pestle.				

N = number of burn tests in set.

av = average burning time of set of N burning times.

SD = standard deviation of set of N burning times.

Heater wire was of composition, 80% nickel and 20% chromium, length, 30 cm, and diameter, 1.016 mm.

Resistance of heater wire was 0.4 Ω .

Table F-2.—Oxidizers Tested by UN Procedure

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
50	NH ₄ NO ₃	Cellulose	1/1	71
51	"	"	1/1	70
52	"	"	1/1	81
53	"	"	1/1	76
54	"	"	1/1	80
For the above test set: N = 5, av = 75 s, and SD = 5 s. SCO was ground using a mortar and pestle.				
46	NH ₄ NO ₃	Cellulose	4/1	180
47	"	"	4/1	152
48	"	"	4/1	183
49	"	"	4/1	167
55	"	"	4/1	147
For the above test set: N = 5, av = 166 s, and SD = 16 s. SCO was ground using a mortar and pestle.				
287	NH ₄ ClO ₄	Cellulose	1/1	31
294	"	"	1/1	29
295	"	"	1/1	39
296	"	"	1/1	50
297	"	"	1/1	39
For the above test set: N = 5, av = 38 s, and SD = 8 s. Particle size range for above test set is 0 mm to 0.3 mm.				
298	NH ₄ ClO ₄	Cellulose	1/1	43
299	"	"	1/1	42
300	"	"	1/1	52
301	"	"	1/1	47
302	"	"	1/1	47
303	"	"	1/1	46
For the above test set: N = 6, av = 46 s, and SD = 4 s. Particle size range for above test set is 0 mm to 0.3 mm.				

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
288	NH_4ClO_4	Cellulose	4/1	13.4
289	"	"	4/1	15.5
290	"	"	4/1	17.2
291	"	"	4/1	19.2
292	"	"	4/1	18.2

For the above test set: $N = 5$, $av = 16.7$ s, and $SD = 2.3$ s.

Particle size range for above test set is 0 mm to 0.3 mm.

293	NH_4ClO_4	Cellulose	4/1	18.5
304	"	"	4/1	15.0
305	"	"	4/1	16.5
306	"	"	4/1	15.0
307	"	"	4/1	13.3

For the above test set: $N = 5$, $av = 15.7$ s, and $SD = 2.0$ s.

Particle size range for above test set is 0 mm to 0.3 mm.

308	NH_4ClO_4	Basswood	4/1	24.0
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For the above test, the particle size range is 0 mm to 0.3 mm.

The UN wire configuration and timing procedure were used for the above test.

354	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	Cellulose	4/1	>180
355	"	"	4/1	>180

For the above test set: $N = 2$, av is greater than 180 s.

Particle size range for above two tests is for chemical, Aldrich Cat. No. 21,558-9, from its bottle.

97	$\text{Ca}(\text{ClO})_2$	Cellulose	1/1	85
98	"	"	1/1	72
99	"	"	1/1	95
100	"	"	1/1	70
102	"	"	1/1	90

For the above test set: $N = 5$, $av = 82$ s, and $SD = 11$ s.

SCO was ground using a mortar and pestle.

245	$\text{Ca}(\text{ClO})_2$	Cellulose	1/1	>180 (Suspect)
246	"	"	1/1	>180 (Suspect)
247	"	"	1/1	>180 (Suspect)

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
248	"	"	1/1	>180 (Suspect)
249	"	"	1/1	>180 (Suspect)
250	"	"	1/1	>180 (Suspect)
251	"	"	1/1	>180 (Suspect)
252	"	"	1/1	>180 (Suspect)
253	"	"	1/1	>180 (Suspect)
254	"	"	1/1	>180 (Suspect)
For the above test set: N = 10, av is greater than 180 s. Particle size range for above test set is 0 mm to 0.3 mm. Average burning time, av, for above test set is suspect. This set of tests needs to be redone with fresh chemical.				
406	Ca(ClO) ₂	Cellulose	1/1	50
407	"	"	1/1	65
408	"	"	1/1	60
409	"	"	1/1	60
410	"	"	1/1	66
For the above test set: N = 5, av = 60 s, and SD = 6 s. Particle size range for above test set is for the chemical, Fisher Cat. No. C100-500, from its bottle.				
92	Ca(ClO) ₂	Cellulose	4/1	8.5
93	"	"	4/1	8.0
94	"	"	4/1	8.0
95	"	"	4/1	9.0
96	"	"	4/1	10.0
For the above test set: N = 5, av = 8.7 s, and SD = 0.8 s. SCO was ground using a mortar and pestle.				
235	Ca(ClO) ₂	Cellulose	4/1	4.9
236	"	"	4/1	6.5
237	"	"	4/1	5.8
238	"	"	4/1	6.5
239	"	"	4/1	6.5

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
For the above test set: N = 5, av = 6.0 s, and SD = 0.7 s. Particle size range for above test set is 0 mm to 0.3 mm.				
240	Ca(ClO) ₂	Cellulose	4/1	5.3
241	"	"	4/1	7.5
242	"	"	4/1	5.2
243	"	"	4/1	5.2
244	"	"	4/1	5.5
For the above test set: N = 5, av = 5.7 s, and SD = 1.0 s. Particle size range for above test set is 0 mm to 0.3 mm.				
411	Ca(ClO) ₂	Cellulose	4/1	19.2
412	"	"	4/1	28.0
413	"	"	4/1	28.0
414	"	"	4/1	27.9
415	"	"	4/1	31.0
For the above test set: N = 5, av = 26.8 s, and SD = 4.5 s. Particle size range for above test set is for the chemical, Fisher Cat. No. C100-500, from its bottle.				
668	Ca(NO ₃) ₂ ·4(H ₂ O)	Cellulose	1/1	82
683	"	"	1/1	121
684	"	"	1/1	70
685	"	"	1/1	80
686	"	"	1/1	65
For the above test set: N = 5, av = 84 s, and SD = 22 s. Particle size range for above test set is 0 mm to 0.3 mm.				
687	Ca(NO ₃) ₂ ·4(H ₂ O)	Cellulose	1/1	82
688	"	"	1/1	70
689	"	"	1/1	67
For the above test set: N = 3, av = 73 s, and SD = 8 s. Particle size range for above test set is 0 mm to 0.3 mm.				
680	Ca(NO ₃) ₂ ·4(H ₂ O)	Cellulose	1/1	128
681	"	"	1/1	>180
682	"	"	1/1	148

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
For above test set (excluding test 681): N = 2, av = 138 s, and SD = 14 s. Particle size range for above test set is for the chemical, Fisher Cat. No. C109-3, from its bottle.				
669	$\text{Ca}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$	Cellulose	4/1	>180 (90 Watts)
670	"	"	4/1	143 (13-s Flame)
671	"	"	4/1	>180 (~No Flaming)
672	"	"	4/1	154 (Smoking End)
673	"	"	4/1	160 " "
674	"	"	4/1	150 " "
For above test set (excluding tests 669 and 671): N = 4, av = 152 s, and SD = 7 s. Particle size range for above test set is 0 mm to 0.3 mm.				
675	$\text{Ca}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$	Cellulose	4/1	160
676	"	"	4/1	145
For above test set: N = 2, av = 152 s, and SD = 11 s. Particle size range for above test set is 0 mm to 0.3 mm.				
677	$\text{Ca}(\text{NO}_3)_2 \cdot 4(\text{H}_2\text{O})$	Cellulose	4/1	148
678	"	"	4/1	140
679	"	"	4/1	120
For the above test set: N = 3, av = 136 s, and SD = 14 s. Particle size range for above test set is for the chemical, Fisher Cat. No. C109-3, from its bottle.				
575	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	Cellulose	1/1	29
576	"	"	1/1	20
577	"	"	1/1	26
578	"	"	1/1	29
579	"	"	1/1	20
For the above test set: N = 5, av = 25 s, and SD = 5 s. Particle size range for above test set is 0 mm to 0.3 mm.				
580	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	Cellulose	1/1	23
581	"	"	1/1	30
582	"	"	1/1	22
583	"	"	1/1	28
584	"	"	1/1	20

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
For the above test set: N = 5, $av = 25$ s, and SD = 4 s. Particle size range for above test set is 0 mm to 0.3 mm.				
565	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	Cellulose	4/1	8.0
566	"	"	4/1	7.2
567	"	"	4/1	6.6
568	"	"	4/1	7.0
569	"	"	4/1	8.0
For the above test set: N = 5, $av = 7.4$ s, and SD = 0.6 s. Particle size range for above test set is 0 mm to 0.3 mm.				
570	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	Cellulose	4/1	7.5
571	"	"	4/1	8.6
572	"	"	4/1	8.9
573	"	"	4/1	8.3
574	"	"	4/1	7.2
For the above test set: N = 5, $av = 8.1$ s, and SD = 0.7 s. Particle size range for above test set is 0 mm to 0.3 mm.				
80	$\text{Mg}(\text{ClO}_4)_2$	Cellulose	1/1	16.7
81	"	"	1/1	15.7
82	"	"	1/1	17.0
83	"	"	1/1	14.3
84	"	"	1/1	12.8
For the above test set: N = 5, $av = 15.3$ s, and SD = 1.8 s. SCO was ground using a mortar and pestle.				
275	$\text{Mg}(\text{ClO}_4)_2$	Cellulose	1/1	12.5
276	"	"	1/1	27.0 (Outlier)
277	"	"	1/1	10.5
278	"	"	1/1	11.0
279	"	"	1/1	13.5
For the above test set: N = 4 (assuming test 276 is an outlier), $av = 11.9$ s, and SD = 1.4 s. Particle size range for above test set is 0 mm to 0.3 mm.				
280	$\text{Mg}(\text{ClO}_4)_2$	Cellulose	1/1	9.8

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
281	"	"	1/1	10.5
282	"	"	1/1	11.0
283	"	"	1/1	13.5
284	"	"	1/1	11.7
For the above test set: N = 5, av = 11.3 s, and SD = 1.4 s. Particle size range for above test set is 0 mm to 0.3 mm.				
359	Mg(ClO ₄) ₂	Cellulose	1/1	24.0
383	"	"	1/1	55.0
384	"	"	1/1	53.3
385	"	"	1/1	61.5
386	"	"	1/1	27.0
For the above test set: N = 5, av = 44.2 s, and SD = 17.3 s. For the above test set, particles were large flakes as received from vendor, Fisher, Cat. No. M54-500.				
387	Mg(ClO ₄) ₂	Cellulose	1/1	16.0
388	"	"	1/1	32.7
389	"	"	1/1	18.0
390	"	"	1/1	18.3
391	"	"	1/1	23.0
For the above test set: N = 5, av = 21.6 s, and SD = 6.7 s. For the above test set, particles were large flakes as received from vendor, Fisher, Cat. No. M54-500.				
402	Mg(ClO ₄) ₂	Basswood	1/1	11.3
403	"	"	1/1	11.5
404	"	"	1/1	14.5
405	"	"	1/1	13.0
For above test set: N = 4, av = 12.6 s, SD = 1.5 s, and UN wire configuration and timing procedure were used. For above test set, particles were large flakes as received from vendor, Fisher, Cat. No. M54-500.				
85	Mg(ClO ₄) ₂	Cellulose	4/1	6.7
86	"	"	4/1	6.3
87	"	"	4/1	7.6
88	"	"	4/1	10.0

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
89	"	"	4/1	6.5
For the above test set: N = 5, $av = 7.4$ s, and $SD = 1.5$ s. SCO was ground using a mortar and pestle.				
265	$Mg(ClO_4)_2$	Cellulose	4/1	8.5
266	"	"	4/1	9.5
267	"	"	4/1	8.7
268	"	"	4/1	7.7
269	"	"	4/1	9.0
For the above test set: N = 5, $av = 8.7$ s, and $SD = 0.7$ s. Particle size range for above test set is 0 mm to 0.3 mm.				
270	$Mg(ClO_4)_2$	Cellulose	4/1	10.3
271	"	"	4/1	9.5
272	"	"	4/1	10.5
273	"	"	4/1	11.3
274	"	"	4/1	11.5
For the above test set: N = 5, $av = 10.6$ s, and $SD = 0.8$ s. Particle size range for above test set is 0 mm to 0.3 mm.				
358	$Mg(ClO_4)_2$	Cellulose	4/1	18.1
381	"	"	4/1	27.0 (Outlier)
382	"	"	4/1	15.0
392	"	"	4/1	8.3
393	"	"	4/1	7.0
For the above test set: N = 4 (assuming test 381 is an outlier), $av = 12.1$ s, and $SD = 5.3$ s. For the above test set, particles were large flakes as received from vendor, Fisher, Cat. No. M54-500.				
393	$Mg(ClO_4)_2$	Cellulose	4/1	7.0
394	"	"	4/1	8.5
395	"	"	4/1	9.5
396	"	"	4/1	10.3
397	"	"	4/1	7.7

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
For the above test set: N = 5, av = 8.6 s, SD = 1.3 s, and particles were large flakes as received from vendor, Fisher, Cat. No. M54-500.				
398	Mg(ClO ₄) ₂	Basswood	4/1	8.9
399	"	"	4/1	7.7
400	"	"	4/1	7.3
401	"	"	4/1	11.1
For above test set: N = 4, av = 8.8 s, SD = 1.7 s, and UN wire configuration and timing procedure were used. For above test set, particles were large flakes as received from vendor, Fisher, Cat. No. M54-500.				
153	KBrO ₃	Cellulose	1/1	21.0
190	"	"	1/1	25.0
191	"	"	1/1	21.9
192	"	"	1/1	19.5
193	"	"	1/1	23.0
For the above test set: N = 5, av = 22.0 s, and SD = 2.1 s. Particle size range for above two tests is 0.15 mm to 0.3 mm.				
229	KBrO ₃	Cellulose	1/1	12.4
230	"	"	1/1	7.6
231	"	"	1/1	6.6
232	"	"	1/1	7.5
233	"	"	1/1	9.3
For the above test set: N = 5, av = 8.7 s, and SD = 2.3 s. Particle size range for above test set is 0 mm to 0.15 mm.				
207	KBrO ₃	Cellulose	4/1	3.8
208	"	"	4/1	3.8
209	"	"	4/1	4.7
210	"	"	4/1	3.6
211	"	"	4/1	4.4
For the above test set: N = 5, av = 4.1 s, and SD = 0.5 s. Particle size range for above test set is 0 mm to 0.15 mm.				
181	KBrO ₃	Cellulose	4/1	6.0

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
182	"	"	4/1	6.4
For both tests above, the mass of the mixture was 15 grams. Particle size range for above two tests is 0.15 mm to 0.3 mm.				
202	KBrO ₃	Cellulose	4/1	6.5
203	"	"	4/1	7.3
204	"	"	4/1	7.5
205	"	"	4/1	5.3
206	"	"	4/1	7.0
For the above test set: N = 5, av = 6.7 s, and SD = 0.9 s. Particle size range for above test set is 0.15 mm to 0.3 mm.				
438	KClO ₃	Cellulose	1/9	150
439	"	"	1/9	156
440	"	"	1/9	138
For the above test set: N = 3, av = 148 s, and SD = 9 s. Particle size range for above test set is 0 mm to 0.3 mm.				
463	KClO ₃	Cellulose	1/7.3	150
464	"	"	1/7.3	112
465	"	"	1/7.3	107
For the above test set: N = 3, av = 123 s, and SD = 24 s. Particle size range for above test set is 0 mm to 0.3 mm.				
466	KClO ₃	Cellulose	1/5.25	41.5
467	"	"	1/5.25	39.0
468	"	"	1/5.25	50.4
For the above test set: N = 3, av = 43.6 s, and SD = 6.0 s. Particle size range for above test set is 0 mm to 0.3 mm.				
441	KClO ₃	Cellulose	1/5	42.2
442	"	"	1/5	44.3
443	"	"	1/5	42.2
For the above test set: N = 3, av = 42.9 s, and SD = 1.2 s. Particle size range for above test set is 0 mm to 0.3 mm.				
428	KClO ₃	Cellulose	3/7	11.0

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
429	"	"	3/7	10.2
430	"	"	3/7	10.5
431	"	"	3/7	10.5
432	"	"	3/7	10.3
For the above test set: N = 5, av = 10.5 s, and SD = 0.3 s. Particle size range for above test set is 0 mm to 0.3 mm.				
433	KClO ₃	Cellulose	2/3	10.2
434	"	"	2/3	8.8
435	"	"	2/3	8.5
436	"	"	2/3	8.9
437	"	"	2/3	9.4
For the above test set: N = 5, av = 9.2 s, and SD = 0.7 s. Particle size range for above test set is 0 mm to 0.3 mm.				
16	KClO ₃	Cellulose	1/1	9.0
22	"	"	1/1	8.1
23	"	"	1/1	7.0
24	"	"	1/1	7.7
25	"	"	1/1	7.8
For the above test set: N = 5, av = 7.9 s, and SD = 0.7 s. SCO was ground using a mortar and pestle.				
505	KClO ₃	Cellulose	1/1	38.5 (Suspect)
506	"	"	1/1	35.3 (Suspect)
507	"	"	1/1	38.1 (Suspect)
For the above test set: N = 3, av = 37.3 s, and SD = 1.7 s. Particle size range for above test set is 0 mm to 0.104 mm. Average for above test set is suspect since KClO ₃ was not from its original bottle and average is considerably greater than average for test set below.				
349	KClO ₃	Cellulose	1/1	7.5
351	"	"	1/1	8.5
355B	"	"	1/1	8.0
553	"	"	1/1	8.3

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
554	"	"	1/1	8.2
For the above test set: $N = 5$, $av = 8.1$ s, and $SD = 0.4$ s. Particle size range for above test set is for Fisher's Catalog No. P210, Laboratory-Grade $KClO_3$ from its bottle. Mass of mixture was 30 g.				
555	$KClO_3$	Cellulose	1/1	7.2
556	"	"	1/1	6.4
For the above test set: $N = 2$, $av = 6.8$ s, and $SD = 0.6$ s. Particle size range for above test set is for Fisher's Catalog No. P210, Laboratory-Grade $KClO_3$ from its bottle. Mass of mixture was 20 g.				
557	$KClO_3$	Cellulose	1/1	6.1
558	"	"	1/1	6.5
For the above test set: $N = 2$, $av = 6.3$ s, and $SD = 0.3$ s. Particle size range for above test set is for Fisher's Catalog No. P210, Laboratory-Grade $KClO_3$ from its bottle. Mass of mixture was 10 g.				
447	$KClO_3$	Cellulose	2/1	4.4
448	"	"	2/1	4.1
449	"	"	2/1	4.7
For the above test set: $N = 3$, $av = 4.4$ s, and $SD = 0.3$ s. Particle size range for above test set is 0 mm to 0.3 mm.				
450	$KClO_3$	Cellulose	2.53/1	3.8
451	"	"	2.53/1	4.3
For the above test set: $N = 2$, $av = 4.1$ s, and $SD = 0.4$ s. Particle size range for above test set is 0 mm to 0.3 mm.				
550	$KClO_3$	Cellulose	2.53/1	5.8
551	"	"	2.53/1	6.9
552	"	"	2.53/1	6.3
For the above test set: $N = 3$, $av = 6.3$ s, and $SD = 0.6$ s. Particle size range for above test set is for Fisher's Catalog No. P210, Laboratory-Grade $KClO_3$ from its bottle.				
564	$KClO_3$	Cellulose	2.53/1	9.3
Particle size range for above test is for the chemical from its bottle. Mass of mixture was 30 g. Circular wire was placed on top of pile and current to wire was maintained during combustion as in UN procedure.				
547	$KClO_3$	Cellulose	2.53/1	6.3

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
548	"	"	2.53/1	7.2
549	"	"	2.53/1	6.5
For the above test set: $N = 3$, $av = 6.7$ s, and $SD = 0.5$ s. Particle size range for above test set is for Fisher's Catalog No. P210, Laboratory-Grade $KClO_3$ from its bottle. Mass of mixture was 20 g.				
544	$KClO_3$	Cellulose	2.53/1	3.6
545	"	"	2.53/1	4.9
546	"	"	2.53/1	2.4
For the above test set: $N = 3$, $av = 3.6$ s, and $SD = 1.2$ s. Particle size range for above test set is for Fisher's Catalog No. P210, Laboratory-Grade $KClO_3$ from its bottle. Mass of mixture was 15 g.				
541	$KClO_3$	Cellulose	2.53/1	6.0
542	"	"	2.53/1	5.9
543	"	"	2.53/1	5.9
For the above test set: $N = 3$, $av = 5.9$ s, and $SD = 0.1$ s. Particle size range for above test set is for Fisher's Catalog No. P210, Laboratory-Grade $KClO_3$ from its bottle. Mass of mixture was 10 g.				
460	$KClO_3$	Cellulose	2.7/1	4.6
461	"	"	2.7/1	5.8
462	"	"	2.7/1	4.9
For the above test set: $N = 3$, $av = 5.1$ s, and $SD = 0.6$ s. Particle size range for above test set is 0 mm to 0.3 mm.				
444	$KClO_3$	Cellulose	3/1	5.1
454	"	"	3/1	5.0
455	"	"	3/1	6.1
456	"	"	3/1	5.8
For the above test set: $N = 4$, $av = 5.5$ s, and $SD = 0.5$ s. Particle size range for above test set is 0 mm to 0.3 mm.				
452	$KClO_3$	Cellulose	3.62/1	5.5
453	"	"	3.62/1	5.0
458	"	"	3.62/1	5.5
459	"	"	3.62/1	5.3

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
For the above test set: N = 4, av = 5.3 s, and SD = 0.2 s. Particle size range for above test set is 0 mm to 0.3 mm.				
17	KClO ₃	Cellulose	4/1	5.0
18	"	"	4/1	2.0 (Suspect)
19	"	"	4/1	3.8
20	"	"	4/1	4.0
21	"	"	4/1	3.2
For the above test set: N = 4 (assuming test 18 is an outlier), av = 4.0 s, and SD = 0.7 s. SCO was ground using a mortar and pestle. No video record exists for these earlier tests.				
446	KClO ₃	Cellulose	4/1	5.8
469	"	"	4/1	5.4
470	"	"	4/1	6.0
For the above test set: N = 3, av = 5.7 s, and SD = 0.3 s. Particle size range for above test set is 0 mm to 0.3 mm.				
350	KClO ₃	Cellulose	4/1	5.0
352	"	"	4/1	5.3
353	"	"	4/1	6.4
356	"	"	4/1	5.7
357	"	"	4/1	6.5
For the above test set: N = 5, av = 5.8 s, and SD = 0.7 s. Particle size range for above test set is for Fisher's Catalog No. P210, Laboratory-Grade KClO ₃ from its bottle.				
563	KClO ₃	Cellulose	4/1	6.0
Particle size range for above test was for Fisher's Catalog No. P210, Laboratory-Grade KClO ₃ from its bottle. Mass of mixture was 30 g.				
561	KClO ₃	Cellulose	4/1	7.2
562	"	"	4/1	6.0
For the above test set: N = 2, av = 6.6 s, and SD = 0.8 s. Particle size range for above test set is for Fisher's Catalog No. P210, Laboratory-Grade KClO ₃ from its bottle. Mass of mixture was 20 g.				
559	KClO ₃	Cellulose	4/1	6.6
560	"	"	4/1	8.9

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
For the above test set: $N = 2$, $av = 7.8$ s, and $SD = 1.6$ s. Particle size range for above test set is for Fisher's Catalog No. P210, Laboratory-Grade $KClO_3$ from its bottle. Mass of mixture was 10 g.				
445	$KClO_3$	Cellulose	5/1	6.5
457	$KClO_3$	Cellulose	9/1	13.3
Particle size range for above two tests is 0 mm to 0.3 mm.				
540	$KClO_3$	None	only pure oxidizer	>60
Particle size range for above test is for Fisher's Catalog No. P210, Laboratory-Grade $KClO_3$ from its bottle. Mass of chemical was 10 g.				
4	KNO_3	Cellulose	1/1	22
7	"	"	1/1	23
8	"	"	1/1	20
9	"	"	1/1	18
10	"	"	1/1	27
For the above test set: $N = 5$, $av = 22$ s, and $SD = 3$ s. SCO was ground using a mortar and pestle.				
107	KNO_3	Cellulose	1/1	29
108	"	"	1/1	28
109	"	"	1/1	25
110	"	"	1/1	25
111	"	"	1/1	25
For the above test set: $N = 5$, $av = 26$ s, and $SD = 2$ s. SCO was ground using a mortar and pestle.				
329	KNO_3	Cellulose	1/1	14
330	"	"	1/1	11
331	"	"	1/1	11
332	"	"	1/1	12
333	"	"	1/1	12
For the above test set: $N = 5$, $av = 12.0$ s, and $SD = 1.0$ s. Particle size range for above test set is 0 mm to 0.3 mm.				
334	KNO_3	Cellulose	1/1	11

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
335	"	"	1/1	12
336	"	"	1/1	11
337	"	"	1/1	12
338	"	"	1/1	12

For the above test set: $N = 5$, $av = 12.0$ s, and $SD = 1.0$ s.
Particle size range for above test set is 0 mm to 0.3 mm.

13	KNO_3	Cellulose	4/1	18
14	"	"	4/1	24
15	"	"	4/1	20
29	"	"	4/1	21
31	"	"	4/1	21

For the above test set: $N = 5$, $av = 21$ s, and $SD = 2$ s.
SCO was ground using a mortar and pestle.

112	KNO_3	Cellulose	4/1	13
113	"	"	4/1	13
114	"	"	4/1	12
115	"	"	4/1	13
116	"	"	4/1	13

For the above test set: $N = 5$, $av = 13.0$ s, and $SD = 0.0$ s.
SCO was ground using a mortar and pestle.

319	KNO_3	Cellulose	4/1	10
320	"	"	4/1	10
321	"	"	4/1	10
322	"	"	4/1	11
323	"	"	4/1	10

For the above test set: $N = 5$, $av = 10.0$ s, and $SD = 0.0$ s.
Particle size range for above test set is 0 mm to 0.3 mm.

324	KNO_3	Cellulose	4/1	10
325	"	"	4/1	11
326	"	"	4/1	10

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
327	"	"	4/1	9
328	"	"	4/1	9
For the above test set: N = 5, av = 10.0 s, and SD = 1.0 s. Particle size range for above test set is 0 mm to 0.3 mm.				
339	KNO ₂	Cellulose	1/1	35
340	"	"	1/1	36
341	"	"	1/1	32
342	"	"	1/1	36
343	"	"	1/1	35
For above test set: N = 5, av = 35 s, and SD = 2 s. Particle size range for above test set is for Fisher's Cat. No. P267-500 chemical from its bottle.				
344	KNO ₂	Cellulose	4/1	11.1
345	"	"	4/1	14.2
346	"	"	4/1	13.0
347	"	"	4/1	12.9
348	"	"	4/1	12.5
For above test set: N = 5, av = 12.7 s, SD = 1.1 s, and particle size range is for Fisher's Cat. No. P267-500 chemical from its bottle.				
511	KClO ₄	Cellulose	2/3	49.5
512	"	"	2/3	46.5
513	"	"	2/3	57.5
For the above test set: N = 3, av = 51.2 s, and SD = 5.7 s. Particle size range for above test set is 0 mm to 0.104 mm.				
34	KClO ₄	Cellulose	1/1	46
35	"	"	1/1	37
36	"	"	1/1	42
37	"	"	1/1	53
43	"	"	1/1	35
For the above test set: N = 5, av = 43 s, and SD = 7 s. SCO was ground using a mortar and pestle.				
505	KClO ₄	Cellulose	1/1	38.5

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
506	"	"	1/1	35.3
507	"	"	1/1	38.1
521	"	"	1/1	27.5
522	"	"	1/1	40.5
For the above test set: N = 5, $av = 36.0$ s, and $SD = 5.1$ s. Particle size range for above test set is 0 mm to 0.104 mm.				
523	KClO ₄	Cellulose	1/1	36.2
524	"	"	1/1	28.0
525	"	"	1/1	41.0
526	"	"	1/1	41.2
527	"	"	1/1	25.0
For the above test set: N = 5, $av = 34.3$ s, and $SD = 7.5$ s. Particle size range for above test set is 0 mm to 0.104 mm.				
508	KClO ₄	Cellulose	2.56/1	11.1
509	"	"	2.56/1	10.7
510	"	"	2.56/1	12.2
For the above test set: N = 3, $av = 11.3$ s, and $SD = 0.8$ s. Particle size range for above test set is 0 mm to 0.104 mm.				
38	KClO ₄	Cellulose	4/1	10.8
39	"	"	4/1	11.8
40	"	"	4/1	11.1
41	"	"	4/1	13.4
42	"	"	4/1	13.5
For the above test set: N = 5, $av = 12.1$ s, and $SD = 1.3$ s. SCO was ground using a mortar and pestle.				
502	KClO ₄	Cellulose	4/1	13.4
503	"	"	4/1	14.8
504	"	"	4/1	18.2
514	"	"	4/1	12.4
515	"	"	4/1	13.1

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
For the above test set: N = 5, av = 14.4 s, and SD = 2.3 s. Particle size range for above test set is 0 mm to 0.104 mm.				
516	KClO ₄	Cellulose	4/1	13.1
517	"	"	4/1	12.9
518	"	"	4/1	14.6
519	"	"	4/1	14.2
520	"	"	4/1	13.0
For the above test set: N = 5, av = 13.6 s, and SD = 0.8 s. Particle size range for above test set is 0 mm to 0.104 mm.				
700	KIO ₄	Cellulose	1/1	5.5
706	"	"	1/1	6.2
707	"	"	1/1	5.8
708	"	"	1/1	6.0
For the above test set: N = 4, av = 5.9 s, and SD = 0.3 s. Particle size range for above test set is 0 mm to 0.3 mm.				
701	KIO ₄	Cellulose	4/1	5.5
702	"	"	4/1	6.0
703	"	"	4/1	6.2
704	"	"	4/1	6.5
705	"	"	4/1	6.2
For the above test set: N = 5, av = 6.1 s, and SD = 0.4 s. Particle size range for above test set is 0 mm to 0.3 mm.				
255	KMnO ₄	Cellulose	1/1	15.2
256	"	"	1/1	13.9
257	"	"	1/1	13.4
258	"	"	1/1	13.5
259	"	"	1/1	13.6
For the above test set: N = 5, av = 13.9 s, and SD = 0.7 s. Particle size range for above test set is 0 mm to 0.3 mm.				
309	KMnO ₄	Cellulose	1/1	13.9
310	"	"	1/1	14.2

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
311	"	"	1/1	14.5
312	"	"	1/1	12.8
313	"	"	1/1	14.4

For the above test set: $N = 5$, $av = 14.0$ s, and $SD = 0.7$ s.
Particle size range for above test set is 0 mm to 0.3 mm.

477	KMnO ₄	Cellulose	1/1	20.7
478	"	"	1/1	22.2
479	"	"	1/1	25.1 (Outlier)
480	"	"	1/1	20.4
481	"	"	1/1	20.6
482	"	"	1/1	21.2

For the above test set: $N = 5$ (assuming test 479 is an outlier), $av = 21.0$ s, and $SD = 0.7$ s. Particle size range for above test set is for Fisher's Cat. No. P279-500 chemical from its bottle.

260	KMnO ₄	Cellulose	4/1	6.4
261	"	"	4/1	6.3
262	"	"	4/1	5.8
263	"	"	4/1	6.3
264	"	"	4/1	6.3

For the above test set: $N = 5$, $av = 6.2$ s, and $SD = 0.2$ s.
Particle size range for above test set is 0 mm to 0.3 mm.

314	KMnO ₄	Cellulose	4/1	7.1
315	"	"	4/1	6.2
316	"	"	4/1	6.9
317	"	"	4/1	6.2
318	"	"	4/1	6.0

For the above test set: $N = 5$, $av = 6.5$ s, and $SD = 0.5$ s.
Particle size range for above test set is 0 mm to 0.3 mm.

471	KMnO ₄	Cellulose	4/1	11.3
472	"	"	4/1	10.3
473	"	"	4/1	11.5

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
474	"	"	4/1	12.7
475	"	"	4/1	10.5
476	"	"	4/1	13.7
For the above test set: N = 6, $av = 11.7$ s, $SD = 1.3$ s, and particle size range is for Fisher's Cat. No. P279-500 chemical from its bottle.				
499	KMnO ₄	Cellulose	6/1	8.5
500	"	"	6/1	8.8
501	"	"	6/1	9.0
For the above test set: N = 3, $av = 8.8$ s, $SD = 0.3$ s, and particle size range is for Fisher's Cat. No. P279-500 chemical from its bottle.				
496	KMnO ₄	Cellulose	7/1	9.0
497	"	"	7/1	9.4
498	"	"	7/1	8.8
For the above test set: N = 3, $av = 9.1$ s, $SD = 0.3$ s, and particle size range is for Fisher's Cat. No. P279-500 chemical from its bottle.				
493	KMnO ₄	Cellulose	8/1	9.5
494	"	"	8/1	10.0
495	"	"	8/1	9.1
For the above test set: N = 3, $av = 9.5$ s, $SD = 0.5$ s, and particle size range is for Fisher's Cat. No. P279-500 chemical from its bottle.				
591	NaClO ₃	Cellulose	1/1	8.6
592	"	"	1/1	10.6
593	"	"	1/1	7.7
594	"	"	1/1	7.8
595	"	"	1/1	6.9
For the above test set: N = 5, $av = 8.3$ s, and $SD = 1.4$ s. Particle size range for above test set is 0 mm to 0.3 mm.				
613	NaClO ₃	Cellulose	1/1	8.2
614	"	"	1/1	13.5
For the above test set: N = 2, $av = 10.8$ s, and $SD = 3.7$ s. Particle size range for above test set is for chemical, Fisher Cat. No. S268-500, from its bottle.				

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
596	NaClO ₃	Cellulose	2/1	5.7
597	"	"	2/1	5.9
598	"	"	2/1	6.0
For the above test set: N = 3, av = 5.9 s, and SD = 0.2 s. Particle size range for above test set is 0 mm to 0.3 mm.				
599	NaClO ₃	Cellulose	3/1	6.0
600	"	"	3/1	7.0
601	"	"	3/1	3.9
For the above test set: N = 3, av = 5.6 s, and SD = 1.6 s. Particle size range for above test set is 0 mm to 0.3 mm.				
602	NaClO ₃	Cellulose	4/1	5.5
603	"	"	4/1	5.5
604	"	"	4/1	6.8
605	"	"	4/1	5.3
606	"	"	4/1	5.4
For the above test set: N = 5, av = 5.7 s, and SD = 0.6 s. Particle size range for above test set is 0 mm to 0.3 mm.				
615	NaClO ₃	Cellulose	4/1	5.8
Particle size range for above test is for chemical, Fisher Cat. No. S268-500, from its bottle.				
361	NaNO ₃	Cellulose	1/1	20.5
371	"	"	1/1	24.5
372	"	"	1/1	22.3
373	"	"	1/1	21.4
374	"	"	1/1	22.5
For the above test set: N = 5, av = 22.2 s, and SD = 1.5 s. Particle size range for above test set is 0 mm to 0.3 mm.				
375	NaNO ₃	Cellulose	1/1	21.9
376	"	"	1/1	21.8
377	"	"	1/1	28.9
378	"	"	1/1	21.6

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
379	"	"	1/1	23.3
For the above test set: N = 5, av = 23.5 s, and SD = 3.1 s. Particle size range for above test set is 0 mm to 0.3 mm.				
360	NaNO ₃	Cellulose	4/1	35.0
362	"	"	4/1	22.0
363	"	"	4/1	29.2
364	"	"	4/1	34.5
365	"	"	4/1	37.5
For the above test set: N = 5, av = 31.6 s, and SD = 6.2 s. Particle size range for above test set is 0 mm to 0.3 mm.				
366	NaNO ₃	Cellulose	4/1	26.0
367	"	"	4/1	34.7
368	"	"	4/1	31.8
369	"	"	4/1	30.7
370	"	"	4/1	28.6
For the above test set: N = 5, av = 30.4 s, and SD = 3.3 s. Particle size range for above test set is 0 mm to 0.3 mm.				
646	NaClO ₄ ·H ₂ O	Cellulose	1/1	17
647	"	"	1/1	25
648	"	"	1/1	23
649	"	"	1/1	24
650	"	"	1/1	24
For the above test set: N = 5, av = 23 s, and SD = 3 s. Particle size range for above test set is 0 mm to 0.3 mm.				
657	NaClO ₄ ·H ₂ O	Cellulose	1/1	55
658	"	"	1/1	50
659	"	"	1/1	54
660	"	"	1/1	45
For the above test set: N = 4, av = 51 s, and SD = 5 s. Particle size range for above test set is for chemical, Fisher Cat. No. S490-500, from its bottle.				
641	NaClO ₄ ·H ₂ O	Cellulose	4/1	12.0

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
642	"	"	4/1	11.0
643	"	"	4/1	11.5
644	"	"	4/1	12.0
645	"	"	4/1	11.5
For the above test set: N = 5, av = 11.6 s, and SD = 0.4 s. Particle size range for above test set is 0 mm to 0.3 mm.				
653	NaClO ₄ ·H ₂ O	Cellulose	4/1	30
654	"	"	4/1	31
655	"	"	4/1	31
656	"	"	4/1	25
For the above test set: N = 4, av = 29 s, and SD = 3 s. Particle size range for above test set is for chemical, Fisher Cat. No. S490-500, from its bottle.				
661	Na ₂ O ₂	Cellulose	1/1	2.0
666	"	"	1/1	1.5
667	"	"	1/1	1.7
For the above test set: N = 3, av = 1.7 s, and SD = 0.2 s. Particle size range for above test set is 0 mm to 0.3 mm.				
616	Na ₂ O ₂	Cellulose	1/1	22
617	"	"	1/1	25
624	"	"	1/1	20
625	"	"	1/1	25
626	"	"	1/1	20
627	"	"	1/1	20
628	"	"	1/1	22
For the above test set: N = 7, av = 22 s, and SD = 2 s. Particle size range for above test set is for chemical, Fisher Cat. No. S363-500, from its bottle.				
662	Na ₂ O ₂	Cellulose	4/1	1.4
663	"	"	4/1	1.8
664	"	"	4/1	3.2
For the above test set: N = 3, av = 2.1 s, and SD = 0.9 s. Particle size range for above test set is 0 mm to 0.3 mm.				

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burning Time, Seconds (s)
619	Na_2O_2	Cellulose	4/1	7
620	"	"	4/1	11
621	"	"	4/1	8
622	"	"	4/1	11
623	"	"	4/1	10

For the above test set: $N = 5$, $av = 9$ s, and $SD = 2$ s.

Particle size range for above test set is for chemical, Fisher Cat. No. S363-500, from its bottle.

N = number of burn tests in set.

av = average burning time of set of N burning times.

SD = standard deviation of set of N burning times.

g = grams.

Heater wire of composition, 80% nickel and 20% chromium, length, 30 cm, and diameter, 1.016 mm, was configured into an indented circle.

Resistance of heater wire was 0.4Ω .

Burning time was measured from switching on 150 W to heater wire until end of smoking or open flaming of main body of conical mixture pile.

Table F-3.—Oxidizers Tested by US Procedure

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burn Time, Seconds (s)
170	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	Basswood	1/1	85.0
171	"	"	1/1	88.0
174	"	"	1/1	85.0
For the above test set: N = 3, av = 86.0 s, and SD = 1.7 s. SCO was ground using a mortar and pestle.				
169	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	Basswood	4/1	56.0
172	"	"	4/1	53.0
173	"	"	4/1	44.0
For the above test set: N = 3, av = 51 s, and SD = 6.2 s. SCO was ground using a mortar and pestle.				
134	$\text{Ca}(\text{ClO})_2$	Basswood	1/1	42.5
135	"	"	1/1	43.7
136	"	"	1/1	62.9
137	"	"	1/1	39.9
138	"	"	1/1	48.3
For the above test set: N = 5, av = 47.5 s, and SD = 9.2 s. SCO was ground using a mortar and pestle.				
422	$\text{Ca}(\text{ClO})_2$	Basswood	1/1	47.5
424	"	"	1/1	42.2
425	"	"	1/1	43
426	"	"	1/1	56.9
427	"	"	1/1	34.8
For the above test set: N = 5, av = 44.9 s, and SD = 8.1 s. Particle size range for above test set is for Fisher Cat. No. C100-500 chemical from its bottle.				
129	$\text{Ca}(\text{ClO})_2$	Basswood	4/1	8.4
130	"	"	4/1	5.1
131	"	"	4/1	8.0
132	"	"	4/1	6.0
133	"	"	4/1	10.5

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burn Time, Seconds (s)
For the above test set: N = 5, av = 7.6 s, and SD = 2.1 s. SCO was ground using a mortar and pestle.				
417	Ca(ClO) ₂	Basswood	4/1	14.4
418	"	"	4/1	8.0
419	"	"	4/1	23.0
420	"	"	4/1	16.5
421	"	"	4/1	13.4
For above test set: N = 5; av = 15.1 s, and SD = 5.4 s. Particle size range for above test set is for Fisher Cat. No. C100-500 chemical from its bottle.				
690	Ca(NO ₃) ₂ ·4(H ₂ O)	Basswood	1/1	66
691	"	"	1/1	69
692	"	"	1/1	52
For the above test set: N = 3, av = 62 s, and SD = 9 s. Particle size range for above test set is 0 mm to 0.3 mm.				
693	Ca(NO ₃) ₂ ·4(H ₂ O)	Basswood	4/1	>180
694	"	"	4/1	>180
695	"	"	4/1	>180
Combustion was unsustainable without presence of current to wire. Particle size range for above test set is 0 mm to 0.3 mm.				
585	(NH ₄) ₂ Ce(NO ₃) ₆	Basswood	1/1	25
586	"	"	1/1	20
587	"	"	1/1	20
For the above test set: N = 3, av = 22 s, and SD = 3 s. Particle size range for above test set is 0 mm to 0.3 mm.				
588	(NH ₄) ₂ Ce(NO ₃) ₆	Basswood	4/1	11.3
589	"	"	4/1	10.0
590	"	"	4/1	12.5
For the above test set: N = 3, av = 11.3 s, and SD = 1.2 s. Particle size range for above test set is 0 mm to 0.3 mm.				
144	Mg(ClO ₄) ₂	Basswood	1/1	6.4
145	"	"	1/1	7.8

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burn Time, Seconds (s)
146	"	"	1/1	8.8
147	"	"	1/1	8.7
148	"	"	1/1	7.0
For the above test set: N = 5, av = 7.7 s, and SD = 1.0 s. SCO was ground using a mortar and pestle.				
744	Mg(ClO ₄) ₂	Basswood	1/1	21.8
745	"	"	1/1	38.6
746	"	"	1/1	36.6
747	"	"	1/1	25.6
For the above test set: N = 4, av = 30.9 s, and SD = 8.0 s. Particle size range for above test set is 0 mm to 0.3 mm. The SCO was dried for several months at 65 °C in a convection oven.				
139	Mg(ClO ₄) ₂	Basswood	4/1	4.4
140	"	"	4/1	7.7
141	"	"	4/1	14.4
142	"	"	4/1	9.9
143	"	"	4/1	4.1
For the above test set: N = 5, av = 8.1 s, and SD = 4.3 s. SCO was ground using a mortar and pestle.				
197	KBrO ₃	Basswood	1/1	31.7
198	"	"	1/1	26.8
199	"	"	1/1	40.5
For the above test set: N = 3, av = 33 s, and SD = 6.9 s. Particle size range for above test set is 0 mm to 0.3 mm.				
715	KBrO ₃	Basswood	1/1	27.0
716	"	"	1/1	24.5
717	"	"	1/1	35.3
718	"	"	1/1	52.5
719	"	"	1/1	21.8
720	"	"	1/1	46.1
721	"	"	1/1	65.0 (Outlier)

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burn Time, Seconds (s)
722	"	"	1/1	77.3 (Outlier)
723	"	"	1/1	32.6
724	"	"	1/1	45.3
For the above test set: $N = 8$ (assuming tests 721 and 722 are outliers), $av = 35.6$ s, and $SD = 11.3$ s. Particle size range for above test set is 0 mm to 0.3 mm. Combining the data from the above two test sets (test #s 197, 198, 199, 715, 716, 717, 718, 719, 720, 723, and 724): $N = 11$, $av = 34.9$ s, and $SD = 10.0$ s.				
200	KBrO ₃	Wood Flour	1/1	26.3
201	"	"	4/1	12.9
Particle size range for above two tests is 0 mm to 0.3 mm.				
194	KBrO ₃	Basswood	4/1	9.9
195	"	"	4/1	7.4
196	"	"	4/1	9.9
For the above test set: $N = 3$, $av = 9.1$ s, and $SD = 1.4$ s. Particle size range for above test set is 0 mm to 0.3 mm.				
725	KBrO ₃	Basswood	4/1	13.0
726	"	"	4/1	9.5
727	"	"	4/1	9.0
728	"	"	4/1	8.3
729	"	"	4/1	13.5
For the above test set: $N = 5$, $av = 10.7$ s, and $SD = 2.4$ s. Particle size range for above test set is 0 mm to 0.3 mm. Combining the data for the above two sets (test #s 194, 195, 196, 725, 726, 727, 728, and 729): $N = 8$, $av = 10.1$, and $SD = 3.4$.				
730	KClO ₃	Basswood	1/1	14
731	"	"	2.53/1	11
732	"	"	5/1	12
733	"	"	1/6.5	91 (Heater Left On)
734	"	"	1/6.5	156
735	"	"	1/6.5	159
736	"	"	1/6.5	154

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burn Time, Seconds (s)
737	"	"	1/6.5	173 (Outlier)
For tests 734 through 736: N = 3, av = 156 s, and SD = 2.5 s. Particle size range for above test set is 0 mm to 0.3 mm.				
119	KNO ₃	Basswood	1/1	19.5
120	"	"	1/1	32.5
121	"	"	1/1	24.4
122	"	"	1/1	24.6
123	"	"	1/1	20.0
For the above test set: N = 5, av = 24.2 s, and SD = 5.2 s. SCO was ground using a mortar and pestle.				
124	KNO ₃	Basswood	4/1	25.4
125	"	"	4/1	24.3
126	"	"	4/1	26.0
127	"	"	4/1	21.2
128	"	"	4/1	18.0
For the above test set: N = 5, av = 23.0 s, and SD = 3.3 s. SCO was ground using a mortar and pestle.				
528	KNO ₂	Basswood	1/1	19.9
529	"	"	1/1	20.5
530	"	"	1/1	22.7
531	"	"	1/1	14.5
532	"	"	1/1	14.0
533	"	"	1/1	18.8
For above test set: N = 6, av = 18.4 s, SD = 3.5 s, and particle size range is for Fisher's Cat. No. P267-500 chemical from its bottle.				
534	KNO ₂	Basswood	4/1	6.3
535	"	"	4/1	8.0
536	"	"	4/1	10.9
537	"	"	4/1	7.1
538	"	"	4/1	19.9 (Outlier)
539	"	"	4/1	8.6

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burn Time, Seconds (s)
For above test set: N = 5 (assuming test 538 is an outlier), av = 8.2 s, SD = 1.8 s, and particle size range is for Fisher's Cat. No. P267-500 chemical from its bottle.				
161	KClO ₄	Basswood	1/1	36
162	"	"	1/1	36
163	"	"	1/1	37
For the above test set: N = 3, av = 36 s, and SD = 1 s. SCO was ground using a mortar and pestle.				
738	KClO ₄	Basswood	1/1	42.0 (Heater wire left on)
739	"	"	1/1	36.5
740	"	"	1/1	35.1
741	"	"	1/1	36.5
742	"	"	1/1	41.4
743	"	"	1/1	42.7
For the above test set: N = 6, av = 39.0 s, and SD = 3.4 s. Particle size range for above test set is 0 mm to 0.3 mm.				
164	KClO ₄	Basswood	4/1	14.0
165	"	"	4/1	14.0
166	"	"	4/1	14.0
For the above test set: N = 3, av = 14.0 s, and SD = 0.0 s. SCO was ground using a mortar and pestle.				
709	KIO ₄	Basswood	2.5/1	4.9
Mass of mixture was 21 g. Particle size range for above test set is 0 mm to 0.3 mm.				
710	KIO ₄	Basswood	1/1	5.0
711	"	"	1/1	6.5
For the above test set: N = 2, av = 5.8 s, and SD = 1.1 s. Particle size range for above test set is 0 mm to 0.3 mm.				
712	KIO ₄	Basswood	4/1	6.4
713	"	"	4/1	7.2
714	"	"	4/1	7.8

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burn Time, Seconds (s)
For the above test set: $N = 3$, $av = 7.1$ s, and $SD = 0.7$ s. Particle size range for above test set is 0 mm to 0.3 mm.				
483	KMnO ₄	Basswood	1/1	13.8
484	"	"	1/1	18.1
485	"	"	1/1	99.1 (Outlier)
486	"	"	1/1	22.9
487	"	"	1/1	13.1
For above test set: $N = 4$ (assuming test 485 is an outlier), $av = 17.0$ s, $SD = 4.5$ s, and particle size range is for Fisher's Cat. No. P279-500 chemical from its bottle.				
488	KMnO ₄	Basswood	4/1	6.7
489	"	"	4/1	5.4
490	"	"	4/1	8.2
491	"	"	4/1	6.4
492	"	"	4/1	6.2
For above test set: $N = 5$, $av = 6.6$ s, $SD = 1.0$ s, and particle size range is for Fisher's Cat. No. P279-500 chemical from its bottle.				
610	NaClO ₃	Basswood	1/1	15.3
611	"	"	1/1	16.0
612	"	"	1/1	17.0
For the above test set: $N = 3$, $av = 16.1$ s, and $SD = 0.9$ s. Particle size range for above test set is 0 mm to 0.3 mm.				
607	NaClO ₃	Basswood	4/1	7.4
608	"	"	4/1	7.0
609	"	"	4/1	5.4
For the above test set: $N = 3$, $av = 6.6$ s, and $SD = 1.1$ s. Particle size range for above test set is 0 mm to 0.3 mm.				
629	NaClO ₃	Basswood	1/1	16.5
630	"	"	1/1	11.0
631	"	"	1/1	15.9
For above test set: $N = 3$, $av = 14.5$ s, $SD = 3.0$ s, and particle size range for above test set is for chemical, Fisher Cat. No. S268-500, from its bottle.				

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burn Time, Seconds (s)
749	NaNO_3	Basswood	1/1	21.5
750	"	"	1/1	20.2
751	"	"	1/1	14.5
752	"	"	1/1	23.0
753	"	"	1/1	16.6
For above test set: $N = 5$, $av = 19.2$ s, $SD = 3.5$ s. Particle size range for above test set is 0 mm to 0.3 mm.				
635	$\text{NaClO}_4 \cdot \text{H}_2\text{O}$	Basswood	1/1	19.2
636	"	"	1/1	12.5
637	"	"	1/1	20.2
For above test set: $N = 3$, $av = 17.3$ s, $SD = 4.2$ s, and particle size range is for chemical, Fisher Cat. No. S490-500, from its bottle.				
638	$\text{NaClO}_4 \cdot \text{H}_2\text{O}$	Basswood	4/1	13.0
639	"	"	4/1	14.4
640	"	"	4/1	7.6
651	"	"	4/1	13.0
652	"	"	4/1	13.0
For above test set: $N = 5$, $av = 12.2$ s, $SD = 2.6$ s, and particle size range is for chemical, Fisher Cat. No. S490-500, from its bottle.				
665	Na_2O_2	Basswood	1/1	1.5
Particle size range for above test set is 0 mm to 0.3 mm.				
664	Na_2O_2	Basswood	4/1	1.4
Particle size range for above test set is 0 mm to 0.3 mm.				
629	Na_2O_2	Basswood	1/1	16.5
630	"	"	1/1	11.0
631	"	"	1/1	15.9
For above test set: $N = 3$, $av = 14.5$ s, $SD = 3.0$ s, and particle size range is for chemical, Fisher Cat. No. S363-500, from its bottle.				
618	Na_2O_2	Basswood	4/1	8.5
632	"	"	4/1	9.8
633	"	"	4/1	7.3

Test Number	SCO	Fuel	SCO/Fuel Weight Ratio	Burn Time, Seconds (s)
634	"	"	4/1	10
For above test set: $N = 4$, $av = 7.7$ s, $SD = 1.9$ s, and particle size range is for chemical, Fisher Cat. No. S363-500, from its bottle.				

N = number of burn tests in set.

av = average burning time of set of N burning times.

SD = standard deviation of set of N burning times.

g = grams.

Heater wire of composition, 80% nickel and 20% chromium, length, 30 cm, and diameter, 1.016 mm, was configured into a circle.

Resistance of heater wire was 0.4 Ω .

Temperature of heater wire in open air was about 1,000 °C.

Burning time was measured from start of burning until end of smoking or open flaming of main body of conical mixture pile.

Table F-4.—Oxidizers tested with wood flour, yellow pine, and cellulose

Test No.	SCO	Fuel	O:F, Mass Ratio	Burn Time (from start of application of heat) Sec.	Wire Temp °C	Current, Amperes	Power Watts	Wire Shape
1F	KNO ₃	Wood flour	1/1	60	850	6.3	63.5	US
12F	"	"	1/1	60	760	5.5	48.4	"
13F	"	"	1/1	70	780	5.8	53.8	"
14F	"	"	1/1	30	898	6.8	74.0	"
15F	"	"	1/1	40	808	6.0	57.6	"
16F	"	"	1/1	45	780	5.8	53.8	"
18F	"	"	1/1	40	740	5.4	46.7	"
9F	"	"	1/1	30	700	5.0	40.0	"
10F	"	"	1/1	30	650	4.5	32.4	"
11F	"	"	1/1	30	600	4.0	25.6	"
12F	"	"	1/1	45	560	3.6	20.7	"
13F	"	"	1/1	46	560	3.6	20.7	"
14F	"	"	1/1	53	540	3.4	18.5	"
15F	"	"	0	705	560	3.6	20.7	"
16F	"	Yellow pine	1/1	59	560	3.6	20.7	"
17F	"	"	1/1	22	750	4.5	32.4	"
18F	"	"	1/1	16	700	5.0	40.0	"
19F	"	Wood flour	1/1	29	740	5.4	46.7	"
20F	"	"	1/1	21	760	5.6	50.2	"
21F	"	"	1/1	24	760	5.6	50.2	"
22F	"	"	1/1	29	740	5.4	46.7	"
23F	"	"	1/1	37	600	4.0	25.6	"
24F	"	"	1/1	40	600	4.0	25.6	"

Test No.	SCO	Fuel	O:F, Mass Ratio	Burn Time (from start of application of heat) Sec.	Wire Temp °C	Current, Amperes	Power Watts	Wire Shape
25F	"	"	4/1	116	600	4.0	25.6	"
26F	"	"	1/1	47	560	3.6	20.7	"
27F	"	"	1/1	49	560	3.6	20.7	"
28F	"	"	4/1	116	560	3.6	20.7	"
29F	"	"	4/1	47	700	5.0	40.0	"
30F	"	"	4/1	35	760	5.6	50.2	"
31F	"	"	4/1	45	760	5.6	50.2	"
32F	"	"	4/1	55	760	5.6	50.2	"
33F	"	Yellow pine	4/1	46	700	5.0	40.0	"
34F	"	"	1/1	20	700	5.0	40.0	"
35F	"	Wood flour	1/1	60	600	4.0	25.6	"
36F	"	"	1/1	43	600	4.0	25.6	"
37F	"	Yellow Pine	4/1	34	700	5.0	40.0	"
38F	"	"	4/1	35	700	5.0	40.0	"
39F	"	"	4/1	42	700	5.0	40.0	"
40F	"	Wood flour	4/1	36	700	5.0	40.0	"
41F	"	"	4/1	54	700	5.0	40.0	"
42F	"	"	4/1	60	700	5.0	40.0	"
43F	"	"	4/1	80	700	5.0	40.0	"
44F	"	Cellulose	4/1	30	700	5.0	40.0	"
45F	"	"	4/1	38	700	5.0	40.0	"
46F	"	"	4/1	15	1180	9.4	141	UN
47F	"	"	1/1	15	1180	9.4	141	"
48F	"	"	1/1	20	1190	9.5	144	"

Test No.	SCO	Fuel	O:F, Mass Ratio	Burn Time (from start of application of heat) Sec.	Wire Temp °C	Current, Amperes	Power Watts	Wire Shape
49F	$\text{Ca}(\text{NO}_3)_2$	"	4/1	300	1190	9.5	144	"
50F	"	"	1/1	Wire broke	1190	9.5	144	"
51F	"	"	1/1	"	1190	9.5	144	"
52F	"	"	1/1	90	1190	9.5	144	"

¹ Suspect values because of large scatter with these seven initial tests.
 AWG 24 wire had length, 30 cm; diameter, 0.511 mm; and resistance, 1.6 Ω .

Table F-5.--Comparison between UN and US burning times

	Size	UN, SCO/Fuel						US, SCO/Fuel					
		1/1			4/1			1/1			4/1		
SCO	μm	av, s	SD, s	n	av, s	SD, s	n	av, s	SD, s	n	av, s	SD, s	n
NH ₄ NO ₃	M&P	75	5.0	5	166	16.0	5						
NH ₄ ClO ₄	<300	38	8.0	5	16.7	2.3	5						
	<300	46	4.0	6	15.7	2.0	5						
(NH ₄) ₂ S ₂ O ₈	M&P							86.0	1.7	3	51.0	6.2	3
	Bottle				>180		2						
Ca(ClO) ₂	M&P	82	11.0	5	8.7	0.8	5	47.5	9.2	5	7.6	2.1	5
	<300	>180		5	6.0	0.7	5						
	<300	>180		5	5.7	1.0	5						
	Bottle	60	6.0	5	26.8	4.5	5	44.9	8.1	5	15.1	5.4	5
Ca(NO ₃) ₂ ·4(H ₂ O)	<300	84	22.0	5	152	7.0	4	62.0	9.0	3	>180		3
	<300	73	8.0	3	152	11.0	2						
	Bottle	138	14.0	2	136	14.0	3						
(NH ₄) ₂ Ce(NO ₃) ₆	<300	25	5.0	5	7.4	0.6	5	22.0	3.0	3	11.3	1.2	3
	<300	25	4.0	5	8.1	0.7	5						
Mg(ClO ₄) ₂	M&P	15.3	1.8	5	7.4	1.5	5	7.7	1.0	5	8.1	4.3	5
	<300	11.9	1.4	4	8.7	0.7	5						
	<300	11.3	1.4	5	10.6	0.8	5						

	Size	UN, SCO/Fuel						US, SCO/Fuel					
		1/1			4/1			1/1			4/1		
		av, s	SD, s	n	av, s	SD, s	n	av, s	SD, s	n	av, s	SD, s	n
SCO	µm												
	Bottle	44.2	17.3	5	12.1	5.3	4						
	Bottle	21.6	6.7	5	8.6	1.3	5						
KBrO ₃	M&P	22.0	2.1	5									
	<150	8.7	2.3	5	4.1	0.5	5						
	>150 and <300				6.7	0.9	5						
	<300							34.9	10.0	11	10.1	3.4	8
KClO ₃	M&P	7.9	0.7	5	4.0	0.7	4						
	<300				5.7	0.3	3	14.0	0.0	1			
	Bottle	8.1	0.4	5									
KNO ₃	M&P	22	3.0	5	21	2.0	5	24.2	5.2	5	23.0	3.3	5
	M&P	30	2.0	5	17	1.0	5						
	<300	13.3	1.6	5	13.5	0.3	5						
	<300	12.5	1.1	5	14.3	1.2	5						
KNO ₂	<300	35	2.0	5	12.7	1.1	5						
	Bottle							18.4	3.5	6	8.2	1.8	5
KClO ₄	M&P, <104	43	7.0	5	12.1	1.3	5	36.0	1.0	3	14.0	0.0	3
	<104	36.0	5.1	5	14.4	2.3	5						

SCO	Size	UN, SCO/Fuel						US, SCO/Fuel					
		1/1			4/1			1/1			4/1		
		av, s	SD, s	n	av, s	SD, s	n	av, s	SD, s	n	av, s	SD, s	n
	<104	34.3	7.5	5	13.6	0.8	5						
	<300							39.0	3.4	6			
KIO ₄	<300	5.9	0.3	4	6.1	0.4	5	5.8	1.1	2	7.1	0.7	3
KMnO ₄	<300	13.9	0.7	5	6.2	0.2	5						
	<300	14.0	0.7	5	6.5	0.5	5						
	Bottle	21.0	0.7	5	11.7	1.3	6	17.0	4.5	4	6.6	1.0	5
NaClO ₃	<300	8.3	1.4	5	5.7	0.6	5	16.1	0.9	3	6.6	1.1	3
	Bottle	10.8	3.7	2	5.8	0.0	1	14.5	3.0	3			
NaNO ₃	<300	22.2	1.5	5	31.6	6.2	5						
	<300	23.5	3.1	5	30.4	3.3	5	19.2	3.5	5			
NaClO ₄ ·H ₂ O	<300	23	3.0	5	11.6	0.4	5						
	Bottle	51	5.0	4	29	3.0	4	17.3	4.2	3	12.2	2.6	5
Na ₂ O ₂	<300	1.7	0.2	3	2.1	0.9	3	1.5	0.0	1	1.4	0.0	1
	Bottle	22	2.0	7	9	2.0	5	14.5	3.0	3	7.7	1.9	4

μm = micrometers.

av = average burning time of set of n burning times.

SD = standard deviation of set of n burning times.

n = number of burn tests in set.

s = seconds.

M&P = mortar and pestle grinding of agglomerated particles.

Bottle = particle size of SCO as shipped from its manufacturer.

*****APPENDIX G:****Table of Oxidizer Mass-Fractional-Size Distributions**

Table G-1.--SCO mass-fractional-size distributions

Item	SCO	Size Range, μm	Mass Fraction
1	NH_4NO_3 , Ground prills from Fisher Scientific	> 500	0.724
	"	300 to 500	0.163
	"	150 to 300	0.102
	"	75 to 150	0.012
	"	0 to 75	0
2	$(\text{NH}_4)_2\text{S}_2\text{O}_8$, Aldrich Chemical Company	> 500	0.140
	"	300 to 500	0.455
	"	150 to 300	0.356
	"	75 to 150	0.048
	"	0 to 75	0
3	$\text{Ca}(\text{ClO})_2$, Fisher Scientific	> 500	0.591
	"	300 to 500	0.152
	"	150 to 300	0.095
	"	75 to 150	0.067
	"	0 to 75	0.095
4	$\text{Mg}(\text{ClO}_4)_2$, Fisher Scientific	> 500	0.146
	"	300 to 500	0.196
	"	150 to 300	0.367
	"	75 to 150	0.209
	"	0 to 75	0.082
5	KBrO_3 , Fisher Scientific	> 300	0.413
	"	150 to 300	0.419
	"	< 150	0.168
6	KClO_3 , Fisher Scientific	> 500	0.162
	"	300 to 500	0.179
	"	150 to 300	0.282

Table G-1.--SCO mass-fractional-size distributions

Item	SCO	Size Range, μm	Mass Fraction
	"	75 to 150	0.231
	"	0 to 75	0.145
7	KClO ₄ , Service Chemical Company	> 500	0.024
	"	300 to 500	0.220
	"	150 to 300	0.377
	"	75 to 150	0.291
	"	0 to 75	0.089
8	KClO ₄ , Aldrich Chemical Co.	180 to 300	0.203
	Cat Nbr. 24,183-0, 100-gram bottle	150 to 180	0.183
	"	106 to 150	0.260
	"	< 106	0.354
9	KMnO ₄ , Fisher Scientific, Coarse Crystals	> 500	0.770
	"	300 to 500	0.154
	"	150 to 300	0.069
	"	75 to 150	0.007
	"	0 to 75	0
10	KMnO ₄ , Fisher Scientific, Fine Crystals	> 500	0
	"	300 to 500	0.002
	"	150 to 300	0.873
	"	75 to 150	0.124
	"	0 to 75	0

*****APPENDIX H:****Statistical Criteria for Rejection of Outliers
and Statistical Inference Procedures for Comparing Means and Standard Deviations**

How to compare means and handle outliers (also called stragglers or extreme values) in classification work needs to be addressed. If an outlier is rejected from a set of three measurements, there could be a problem in gaining acceptance of the decision. Using a sample size of two to estimate the standard deviation in the mean burning time can result in a high estimate of the standard deviation of the burning time. The expected larger standard deviation associated with a three-sample test set, as opposed to that with a five-sample test set, would make hypothesis testing of means less confident in the case of three-sample test sets. It may be better to spend more money and an additional hour or two of laboratory effort to conduct several more tests (at least five in total) to reduce experimental uncertainty and provide an improved basis for the rejection of an outlier should such occur than to simplify the work load by doing the minimum effort. Considering the range of magnitudes of the standard deviations in SCO tests and the ease with which the tests can be conducted, one might effectively argue that a sample size of 10 should have been used rather than the five called for by the current UN procedure.

Consideration should be given to evaluating whether the t-test should be employed in SCO test protocol to compare mean burn time for the material being classified with the mean burn time for the appropriate reference standards. **This entails (1) confirming that a correct statistical basis exists for comparing the SCO means by use of the t-distribution and (2), selecting the appropriate levels of significance (α) to use. There is a need to (1) identify a statistical criterion for rejection of an outlier that would have wide spread acceptability in the science community and (2) establish criteria to determine whether additional tests are needed and, if so, how many.**

It would appear that both the establishment of the number of three in the US test protocol and the establishment of five in the UN test protocol did not fully take into account the role played by the standard deviation in comparing means. No mention appears in either the US or UN procedure of the role of the standard deviation in making classification decisions based on a comparison of means.

The decision making process in classification work can be strengthened by adopting standard statistical procedures such as those used in the medical, chemical, physical, biological, economic, social, and psychological areas. A decision process that specifies as the level of significance that which is

typically used in the science community ought to be pursued. Consideration ought to be given also to the use of the F-test for comparing standard deviations associated with the means. Confidence intervals for the appropriate SCO statistical parameters ought to be used to better characterize test results. An excellent account of extreme values with references to original research publications on how to deal with them has been included (PR 16) in E. S. Keeping's undergraduate textbook entitled Introduction to Statistical Inference, Dover Publications (originally published by D. Van Nostrand, 1962). (See pages 199-202 and 213 of Keeping's book.)

For an analysis of the distribution of extreme values where the sample comes from a normal population of known mean and variance, handling of extreme values is a straight forward matter. This case was investigated by Tippett and Pearson who constructed an important table. (See E. S. Pearson and H. O. Hartley, Biometrika Tables for Statisticians, Table 24, Cambridge University Press, 1954 (PR 17) and Table 8.3 in Keeping's book (PR 16).)

When the mean and variance are generally not known, the analysis of stragglers is more complex. This case was analyzed by W. R. Thompson who identified a statistic for a single measurement that has a Student-t distribution with $(N-2)$ degrees of freedom where N denotes the size of the sample. However to implement his findings requires some care. (See W. R. Thompson, "On a Criterion for the Rejection of Observations and the Ratio of the Distribution of Deviation to Sample Standard Deviation," *Annals of Mathematical Statistics*, vol 6, 1935, pp. 214-219 (PR 18) and page 199 of Keeping's book (PR 16).) A practical approach based on a simple ratio criterion for rejection of outliers has been suggested by Dixon. His criterion is dependent upon sample size. (See W. J. Dixon, "Analysis of Extreme Values," *Annals of Mathematical Statistics*, vol 21, 1950, pp 488-506 (PR 19) and W. J. Dixon, "Ratios Involving Extreme Values," *Annals of Mathematical Statistics*, vol 22, 1951, pp 68-78 (PR 20). See also pages 199-200 of Keeping's book (PR 16).)

The range of the sample has been advocated as a tool for estimating the standard deviation of the actual normal population. This technique has been applied to large sample sizes (350 to 550) on down to small sample sizes (5 to 10). For large sample sizes the standard deviation is sometimes estimated as

one sixth of the range. Keeping deals with this technique on pages 200-203 of his book and refers to Tables 23 and 27 in Tippett's book. Although the subject of extremes appears in numerous references dealing with **order statistics**, very few books in English are devoted solely to the subject of extremes. Professor E. J. Gumbel of Columbia University wrote (PR 21) one of the first such books. His book, Statistics of Extremes, was published by Columbia University Press in 1958. The book, meant for statisticians, discusses exact and asymptotic distributions for dealing with extremes. His book emphasizes the use of graphical procedures and provides a 22-page bibliography of the research literature dealing with the analysis of extremes.

*****APPENDIX I:****Graphs of Burning Times of Wood Flour versus Electrical Power**

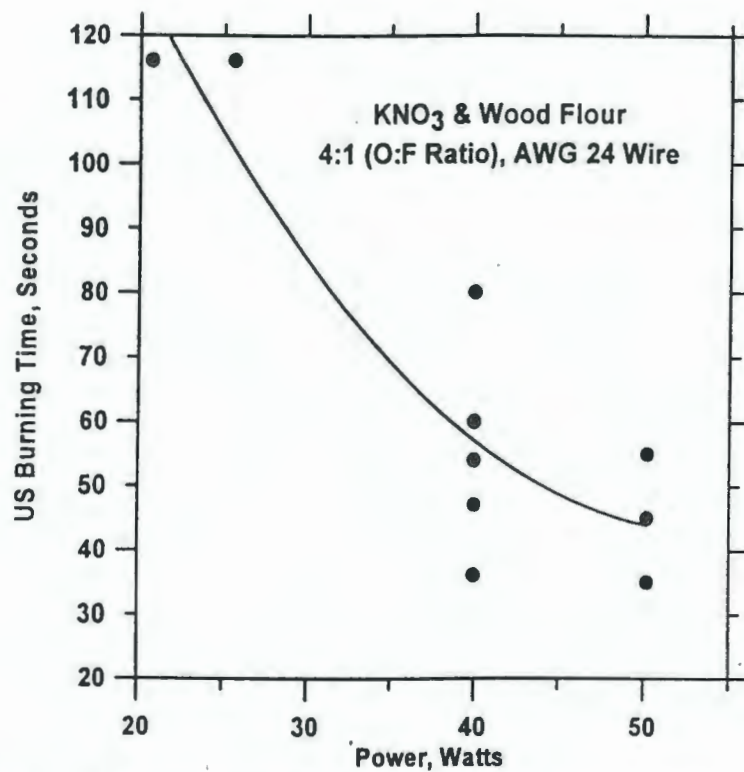


Figure I-1. US mean burning time versus power through AWG 24 ignition wire for 4:1 KNO₃-wood flour mixture

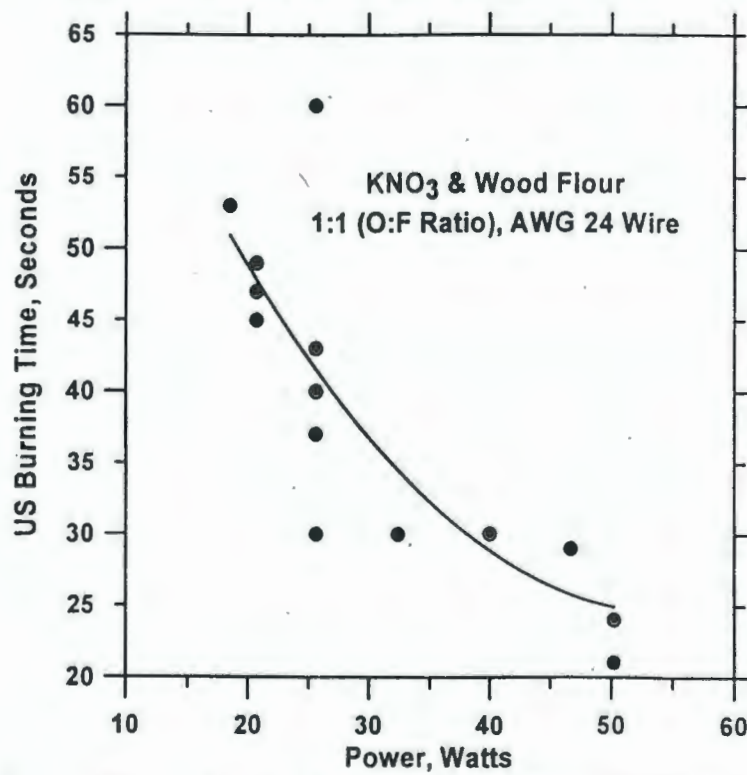


Figure I-2. US mean burning time versus power through AWG 24 ignition wire for 1:1 KNO₃-wood flour mixture

*****APPENDIX J:****Graphs of Ignition Wire Temperature versus Electrical Current**

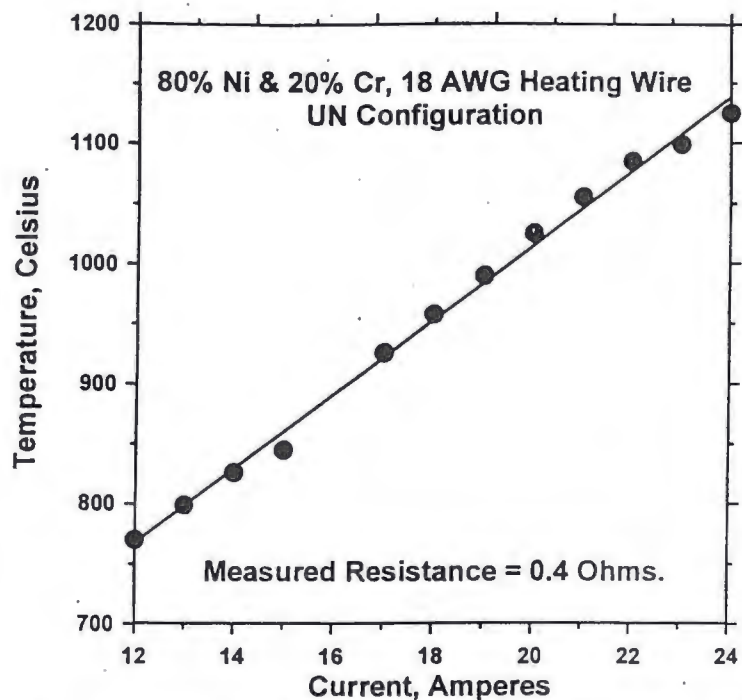


Figure J-1. Temperature of Omega Engineering's 80 % Ni and 20 % Cr AWG 18 ignition wire for UN configuration versus current, 30 cm length

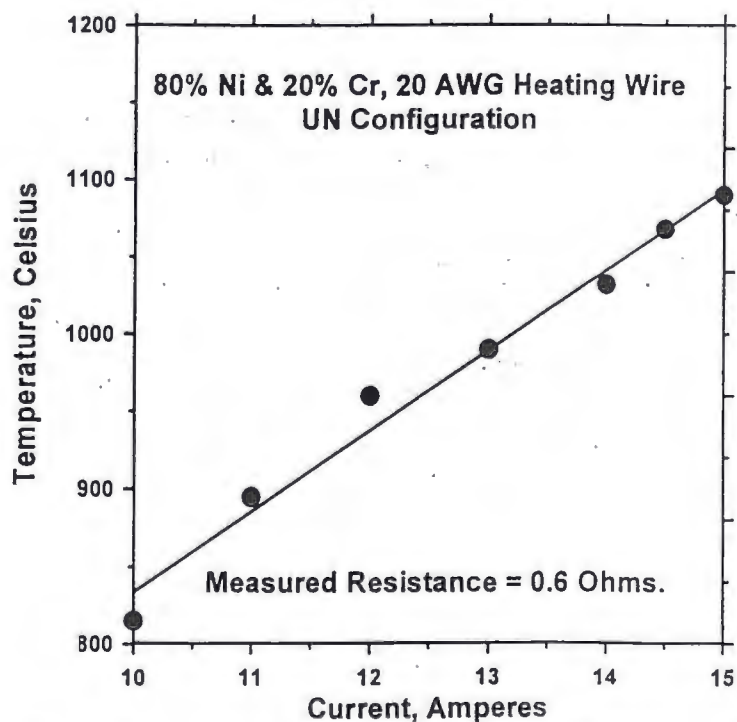


Figure J-2. Temperature of Omega Engineering's 80 % Ni and 20 % Cr AWG 20 ignition wire for UN configuration versus current, 30 cm length

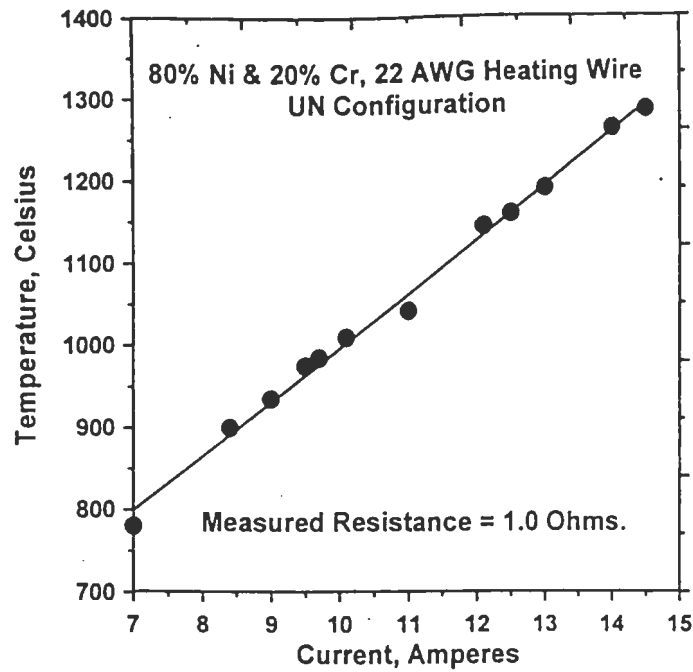


Figure J-3. Temperature of Omega Engineering's 80 % Ni and 20 % Cr AWG 22 ignition wire for UN configuration versus current, , 30 cm length

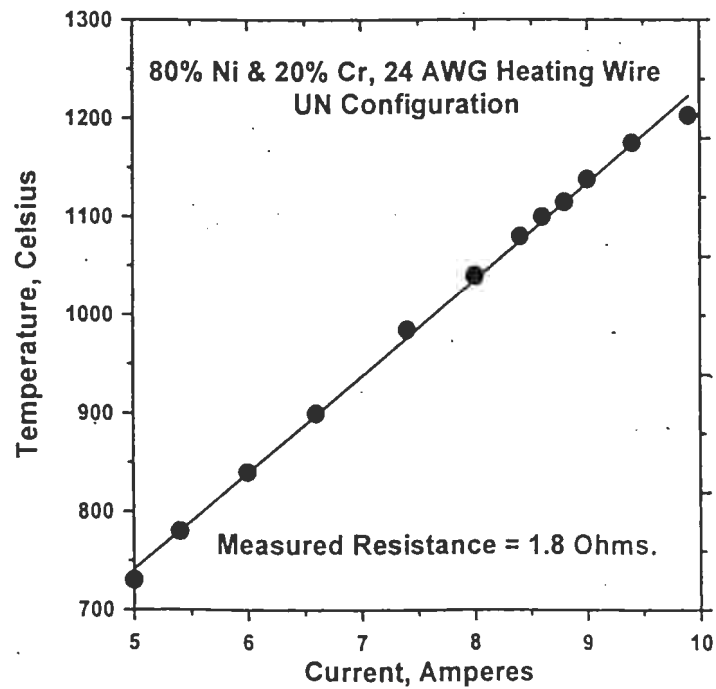


Figure J-4. Temperature of Omega Engineering's 80 % Ni and 20 % Cr AWG 24 ignition wire for UN configuration versus current, 30 cm length

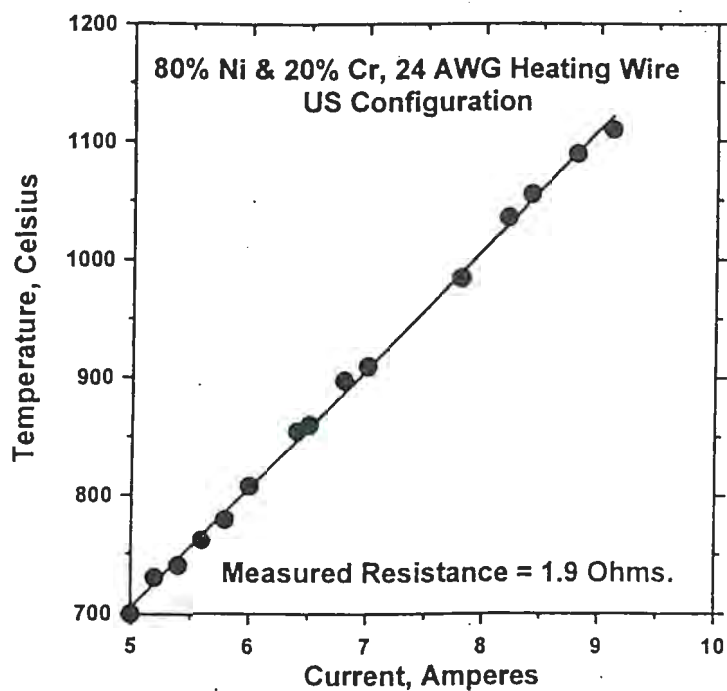


Figure J-5. Temperature of Omega Engineering's 80 % Ni and 20 % Cr AWG 24 ignition wire for US configuration versus current, 30 cm length

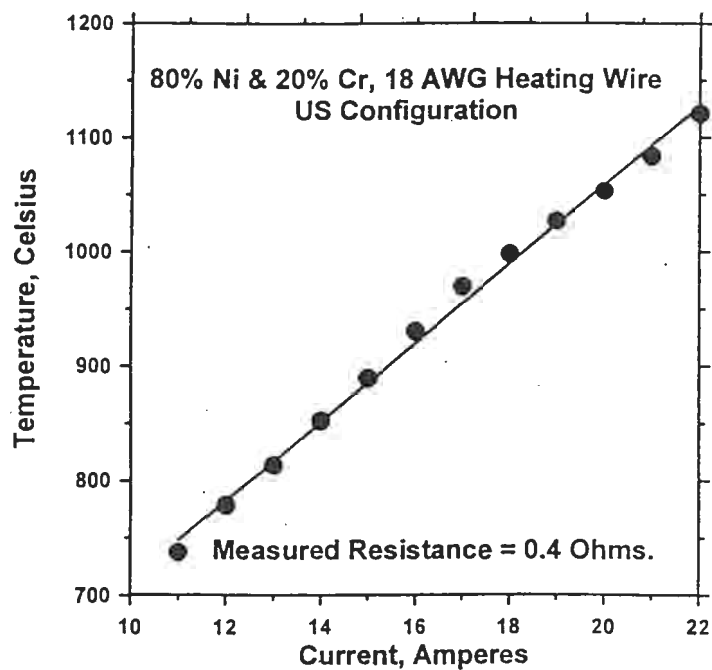


Figure J-6. Temperature of Omega Engineering's 80 % Ni and 20 % Cr AWG 18 ignition wire for US configuration versus current, 30 cm length

*****APPENDIX K:****Hazard Analysis Models**

To evaluate the ability of an exhaust hood to contain the combustion products from rapid and energetic reactions, a hazard assessment model was devised. Chemical models were hypothesized for all the SCO-cellulose reactions. Some of the main variables contributing to the escape of combustion products from the hoods were the (1) the reaction kinetics affected by the particle size distributions and SCO-to-fuel mass ratio, (2) flame temperature related to heats of formation of the reactants and products (tables K-2 through K-4), (3) hood volume, (4) hood gas flow rate, (5) extent of opening of the hood sash, (6) position of reactant mixture relative to the sash opening, and (7) mass of the mixture. Reducing the size of the particles increases the contact area between the SCO and the fuel and increases the speed of the reaction.

**Table K-1.--Calculated stoichiometric SCO-fuel ratios
and masses of reactants**

Item	SCO with Cellulose	Stoichiometric O:F Ratio	Mass of SCO in 30-g Mixture	Mass of Fuel in 30-g Mixture
1	KBrO ₃	4.1	24.1	5.9
2	KClO ₃	3.0	22.5	7.5
3	KClO ₄	2.6	21.7	8.3
4	KIO ₃	5.3	25.2	4.8
5	KIO ₄	4.3	24.3	5.7
6	KMnO ₄	¹ 7.8	26.6	3.4
7	NaClO ₃	2.6	21.7	8.3
8	Na ₂ O ₂	5.8	25.6	4.4

¹ Ratio assumes MnO₂ is only oxide formed.

Table K-2.--Atomic weights of reactant elements

Item	Element	Element's Symbol	Atomic Weight
1	Bromine	Br	79.904
2	Calcium	Ca	40.08
3	Carbon	C	12.011
4	Cerium	Ce	140.12
5	Chlorine	Cl	35.453
6	Hydrogen	H	1.0079
7	Iodine	I	126.9045
8	Magnesium	Mg	24.305
9	Manganese	Mn	54.9380
10	Nitrogen	N	14.0067
11	Oxygen	O	15.9994
12	Potassium	K	39.098
13	Sodium	Na	22.98977
14	Sulfur	S	32.06

Development of Hazard Model for Application to Exhaust Hoods

Consider the chemical equation,



where

SCO denotes solid chemical oxidizer;

$\text{P}_{1(g)}$, $\text{P}_{2(g)}$, $\text{P}_{3(g)}$, and $\text{P}_{4(g)}$ are gaseous products; and

α , β , γ , δ , σ , and μ are the molar coefficients.

Let Δn denote the difference in moles of gases between those formed by the products and reactants. For the above chemical model, $\Delta n = \gamma + \delta + \sigma + \mu$. (EQTN 1)

Consider a mixture of SCO and cellulose ($\text{C}_6\text{H}_{10}\text{O}_5$) of mass M in grams and the mass of SCO to be m_{SCO} . Let the molecular weight of SCO be designated as MW_{SCO} . Let the mass of the fuel be denoted by m_{fuel} . Let the molecular weight of the fuel be denoted by MW_{fuel} .

Let the ambient temperature be T_{amb} in degrees Kelvin – often it is appropriate and convenient to take this value to be 298 °K. Often thermodynamic energy values are tabulated on the basis of temperature being 298 °K. We refer to the choice of T_{amb} as the "cold" condition. We denote the adiabatic flame temperature as T_f in °K. For the rapid and intense open flaming reactions the adiabatic flame temperature usually exceeds 1,700 °K.

Application by Dr. Isaac Zlochower of the NASA - Lewis code for chemical equilibria for the combustion of cellulose with sodium peroxide, potassium chlorate, and potassium bromate gave adiabatic flame temperatures of 1,786 °K, 2,435 °K, and 2,431 °K, respectively. The NASA Lewis CEA code also provided the mole fractions for the likely products. (The NASA - Lewis code has been ported to run in 32-bit FORTRAN on PCs.) At a flame temperature of 1,800 °K, the boiling points of most combustion

products from SCO-cellulose reactions are exceeded. However, there is one important compound whose boiling point exceeds 1,800 °K; it is sodium hydroxide with a boiling point of about 1,900 °K.

For the potassium bromate - cellulose reaction at 2,431 °K the key products in terms of mole fractions are:

$$\text{CO}, \quad X_{\text{CO}} = 0.05$$

$$\text{CO}_2, \quad X_{\text{CO}_2} = 0.33$$

$$\text{H}_2\text{O}, \quad X_{\text{H}_2\text{O}} = 0.30$$

$$\text{KBr}, \quad X_{\text{KBr}} = 0.24$$

$$\text{KOH}, \quad X_{\text{KOH}} = 0.01$$

$$\text{Br}, \quad X_{\text{Br}} = 0.01$$

For the potassium chlorate – cellulose reaction at 2,435 °K the key products in terms of mole fractions are:

$$\text{CO}_2, \quad X_{\text{CO}_2} = 0.33$$

$$\text{H}_2\text{O}, \quad X_{\text{H}_2\text{O}} = 0.29$$

$$\text{KCl}, \quad X_{\text{KCl}} = 0.24$$

$$\text{CO}, \quad X_{\text{CO}} = 0.05$$

$$\text{KOH}, \quad X_{\text{KOH}} = 0.02$$

For the sodium peroxide - cellulose reaction at 1,786 °K the key products in terms of mole fractions are:

$$\text{H}_2\text{O}, \quad X_{\text{H}_2\text{O}} = 0.025$$

$$\text{Na}_2\text{CO}_{3(l)}, \quad X_{\text{Na}_2\text{CO}_{3(l)}} = 0.34$$

$$\text{NaOH}_{(g)}, \quad X_{\text{NaOH}_{(g)}} = 0.276$$

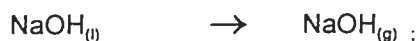
$$\text{NaOH}_{(l)}, \quad X_{\text{NaOH}_{(l)}} = 0.24$$

$$\text{Na}_2\text{O}_{(l)}, \quad X_{\text{Na}_2\text{O}_{(l)}} = 0.068$$

Examination of the Gibbs free energy temperature relationships (by Dr. Zlochower) has indicated (1) that decomposition of sodium carbonate (liquid) to disodium oxide (liquid) and carbon dioxide takes place at above 2,250 °K,



(2) that sodium hydroxide (liquid) is converted appreciably to a gas at greater than 1,900 °K,



and (3) that decomposition of sodium hydroxide (gas) to sodium, oxygen, and water takes place at about 2,450 °K,



Hence, the product species (with the exception of water) being in the liquid state that result from the NASA -Lewis code calculations, are the thermodynamically stable ones for the adiabatic flame temperature °K.

For definiteness in our comparisons of the more energetic oxidizers, let us assume the flame temperature to be 1800 °K and refer to it as the "hot" condition. At 273 °K and 1 atmosphere of pressure, one gram-mole of gas has a volume of 22.414 liters. At an elevation of 305 meters (1,000 ft) above sea level, the standard barometric pressure is 733 mm of Hg rather than 760 mm of Hg.

Let us denote the net change in reaction volume at sea level at temperature T in °K to be V_T . It can be computed when the fuel is in excess from

$$V_T = \left(\frac{m_{SCO}}{MW_{SCO}} \right) \left(\frac{\Delta n}{\alpha} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) \left(\frac{T}{273} \right) \quad (\text{EQTN } 2)$$

When the SCO is in excess, the change in volume can be computed from

$$V_T = \left(\frac{m_{fuel}}{MW_{fuel}} \right) \left(\frac{\Delta n}{\beta} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) \left(\frac{T}{273} \right) \quad (\text{EQTN } 3)$$

Let us denote the oxidizer-fuel mass ratio to be O:F. For intense chemical reactions, the end of combustion occurs at the cessation of open flaming. To facilitate hazard analysis of the more reactive solid chemical oxidizers, we designate the open flaming combustion time in seconds to be $\tau_{O:F}$ for a mixture having an oxidizer-fuel mass ratio, O:F.

Let us denote the rate of change of combustion gas volume with respect to time as

$$Q_T = \frac{dV_T}{d\tau_{O:F}} \quad (\text{EQTN } 4)$$

An approximate value of the volumetric rate can be calculated using the formula

$$Q_T = \frac{dV_T}{d\tau_{O:F}} \cong \left(\frac{V_T}{\tau_{O:F}} \right). \quad (\text{EQTN } 5)$$

If one wishes to normalize the rate of change of production of gases relevant to the hood volume, one can divide the regular production rate by the hood volume. This normalized value given by

$$\hat{Q}_T = \left(\frac{dV_T}{d\tau_{O:F}} \right) / V_{hood} \cong V_T / (V_{hood} \tau_{O:F}). \quad (\text{EQTN } 6)$$

Two hoods of slightly different volumes were used – one hood had a volume of 819 liters and the other 790 liters.

We have at least six parameters - V_{298} , V_{1800} , Q_{298} , $\hat{Q}_{298}$, Q_{1800} , and $\hat{Q}_{1800}$ - that can be used to characterize the dynamics of the reaction. When the fuel is in excess; they are computed from:

$$V_{298} = \left(\frac{m_{SCO}}{MW_{SCO}} \right) \left(\frac{\Delta n}{\alpha} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) \left(\frac{298}{273} \right) =$$

$$\left(\frac{m_{SCO}}{MW_{SCO}} \right) \left(\frac{\Delta n}{\alpha} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) (1.092) \quad ; \quad (\text{EQTN } 7)$$

$$Q_{298} = \frac{dV_{298}}{d\tau_{O:F}} \cong \left(\frac{V_{298}}{\tau_{O:F}} \right) =$$

$$\left(\frac{\left(\frac{m_{SCO}}{MW_{SCO}} \right) \left(\frac{\Delta n}{\alpha} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) (1.092)}{\tau_{O:F}} \right) ; \quad (\text{EQTN } 8)$$

$$\hat{Q}_{298} = \frac{Q_{298}}{V_{hood}} ; \quad (\text{EQTN } 9)$$

$$V_{1800} = \left(\frac{m_{SCO}}{MW_{SCO}} \right) \left(\frac{\Delta n}{\alpha} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) \left(\frac{1800}{273} \right) =$$

$$\left(\frac{m_{SCO}}{MW_{SCO}} \right) \left(\frac{\Delta n}{\alpha} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) (6.59) ; \quad (\text{EQTN } 10)$$

$$Q_{1800} = \frac{dV_{1800}}{d\tau_{O:F}} \cong \left(\frac{V_{1800}}{\tau_{O:F}} \right) =$$

$$\left(\frac{\left(\frac{m_{SCO}}{MW_{SCO}} \right) \left(\frac{\Delta n}{\alpha} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) (6.59)}{\tau_{O:F}} \right) ; \text{ and} \quad (\text{EQTN } 11)$$

$$\hat{Q}_{1800} = \frac{Q_{1800}}{V_{hood}} \quad (\text{EQTN } 12)$$

When the SCO is in excess, the six parameters are computed from

$$V_{298} = \left(\frac{m_{fuel}}{MW_{fuel}} \right) \left(\frac{\Delta n}{\beta} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) \left(\frac{298}{273} \right) =$$

$$\left(\frac{m_{fuel}}{MW_{fuel}} \right) \left(\frac{\Delta n}{\beta} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) (1.092) \quad (\text{EQTN } 13)$$

$$Q_{298} = \frac{dV_{298}}{d\tau_{O:F}} \cong \left(\frac{V_{298}}{\tau_{O:F}} \right) =$$

$$\left(\frac{\left(\frac{m_{fuel}}{MW_{fuel}} \right) \left(\frac{\Delta n}{\beta} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) (1.092)}{\tau_{O:F}} \right) ; \quad (\text{EQTN } 14)$$

$$\hat{Q}_{298} = \frac{Q_{298}}{V_{hood}} ; \quad (\text{EQTN } 15)$$

$$V_{1800} = \left(\frac{m_{fuel}}{MW_{fuel}} \right) \left(\frac{\Delta n}{\beta} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) \left(\frac{1800}{273} \right) =$$

$$\left(\frac{m_{fuel}}{MW_{fuel}} \right) \left(\frac{\Delta n}{\beta} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) (6.59) ; \quad (\text{EQTN } 16)$$

$$Q_{1800} = \frac{dV_{1800}}{d\tau_{O:F}} \cong \left(\frac{V_{1800}}{\tau_{O:F}} \right) =$$

$$\left(\frac{\left(\frac{m_{fuel}}{MW_{fuel}} \right) \left(\frac{\Delta n}{\beta} \right) \left(\frac{22.4 \text{ liters}}{\text{gram mol}} \right) (6.59)}{\tau_{O:F}} \right) ; \text{ and} \quad (\text{EQTN } 17)$$

$$\hat{Q}_{1800} = \frac{Q_{1800}}{V_{hood}} \quad (\text{EQTN } 18)$$

These formulas were applied to eleven different reactions carried out in two different laboratory hoods. **The very energetic peroxide and chlorate reactions overwhelmed the hoods.** Some of the reactions were so violent that one could hear the slamming of the glass sash against its restraining structure. **The sodium peroxide reactions with the SCO being less than 300 μm in size were most intense.** The experimentalists conducted these peroxide tests while standing outside the building and watched the combustion products shoot out of the hood, cross the room for about 5-m and exit through the doorway. The hood's sash had been raised about 20 cm to avoid the shattering of the sash glass by the explosive flame from the rapid reaction involving the < 300 μm sodium peroxide.

The test results for the chemical models are tabulated below. The 819-liter hood was usually overwhelmed when the "Hot" volumetric production rates were in excess of 17 liters/sec. For some hoods

of size 0.8 m^3 , the volumetric flow rate is of the order of $400 \text{ ft}^3/\text{min}$ or 189 liters/sec . This ventilation rate value greatly exceeds the "cold" gas production rate associated with 30-gram mixtures of SCO-cellulose. In rapid explosive flames there is a pressure rise from the gaseous combustion products resulting in directed kinetic energy for products and unreacted components. When an explosive reaction is conducted in a hood, the result is to eject material away from the reaction zone - in some instances material jets through the hood's sash opening out into the work environment. Whether or not the hood is overwhelmed depends upon the:

- (1) Chemical reaction kinetics – particle size distribution and mass ratio of oxidizer to fuel,**
- (2) Adiabatic flame temperature,**
- (3) Mass of reactant mixture,**
- (4) Hood volume,**
- (5) Hood flow rate,**
- (6) Hood sash opening, and**
- (7) Position of reactant mixture relevant to sash opening.**

The reaction time, mixture mass, and adiabatic flame temperature are important factors to take into account. A small particle size greatly increases the rate of production of the gases; and a high flame temperature shifts the products to the gaseous phase increasing the gas pressure. Conditions near stoichiometric usually give the most energetic situation since there is little heat lost by transference to the reactant in excess. A larger hood can more easily handle higher gaseous production rates.

Table K -3.--Chemical models and data for calculating volumetric production rate of gaseous products from reactions
(BASED ON ONE ATMOSPHERE OF PRESSURE - ELEVATION BEING AT SEA LEVEL)

Chemical model (stoichiometric oxidizer to fuel mass ratio)	Mol wt of SCO (moles of SCO)	Mol wt of fuel (moles of fuel)	Mass O:F ratio in 30-gram mix	Burn time, $\tau_{O:F}$ sec	SCO size - M&P, as shipped, or μm	Moles of gas produced per mole of oxidizer, $\left(\frac{\Delta n}{\alpha}\right)$	Moles of gas produced per mole of fuel, $\left(\frac{\Delta n}{\beta}\right)$	"Cold" gas volumetric production rate, Q_{298} liters/sec	Normalized "Cold" gas volumetric production rate, $\frac{Q_{298}}{V_{hood}}$ 1/sec	"Hot" gas volumetric production rate, Q_{1800} liters/sec	Normalized "Hot" gas volumetric production rate, $\frac{Q_{1800}}{V_{hood}}$ 1/sec
$12Na_2O_2 + C_6H_{10}O_5 \rightarrow 6CO_2 + 10NaOH + 7Na_2O$ (5.77)	77.99 (0.192)	162.14 (0.0370)	1:1	1.7	< 300	(23 / 12) = 1.91	(fuel is in excess)	4.8	59×10^{-4}	29.2	356×10^{-4}
$4KClO_3 + C_6H_{10}O_5 \rightarrow 4KCl + 6CO_2 + 5H_2O$ (3.02)	122.55 (0.184)	162.14 (0.0463)	3:1	5.5	< 300	(15 / 4) = 3.75	(fuel is in excess)	2.9	35×10^{-4}	17.4	212×10^{-4}
$4KBrO_3 + C_6H_{10}O_5 \rightarrow 4KBr + 6CO_2 + 5H_2O$ (4.12)	167.00 (0.144)	162.14 (0.0370)	4:1	4.1	< 150	(15 / 4) = 3.75	(fuel is in excess)	3.2	41×10^{-4}	19.4	246×10^{-4}
$3KClO_4 + C_6H_{10}O_5 \rightarrow 3KCl + 6CO_2 + 5H_2O$ (2.56)	138.6 (0.173)	162.14 (0.0370)	4:1	12.1	M&P	(oxidizer is in excess)	(14 / 1) = 14	1.1	13×10^{-4}	6.32	80×10^{-4}

Chemical model (stoichiometric oxidizer to fuel mass ratio)	Mol wt of SCO (moles of SCO)	Mol wt of fuel (moles of fuel)	Mass O:F ratio in 30-gram mix	Burn time, $\tau_{O:F}$ sec	SCO size - M&P, as shipped, or μm	Moles of gas produced per mole of oxidizer, $\left(\frac{\Delta n}{\alpha}\right)$	Moles of gas produced per mole of fuel, $\left(\frac{\Delta n}{\beta}\right)$	"Cold" gas volumetric production rate, Q_{298} liters/sec	Normalized "Cold" gas volumetric production rate, $\frac{Q_{298}}{V_{hood}}$ 1/sec	"Hot" gas volumetric production rate, Q_{1800} liters/sec	Normalized "Hot" gas volumetric production rate, $\frac{Q_{1800}}{V_{hood}}$ 1/sec
$24(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6 + 49\text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 192\text{NH}_3 + 53\text{H}_2\text{O} + 294\text{CO}_2 + 12\text{Ce}_2\text{O}_3$ (1.66)	548.2 (0.0438)	162.14 (0.0370)	4:1	7.4	< 300	(oxidizer is in excess)	(539 / 49) = 11	1.4	17×10^{-4}	8.12	103×10^{-4}
$3\text{Mg}(\text{ClO}_4)_2 + 2\text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 3\text{MgCl}_2 + 10\text{H}_2\text{O} + 12\text{CO}_2$ (2.07)	223.2 (0.108)	162.14 (0.0370)	4:1	8.7	< 300	(oxidizer is in excess)	(25 / 2) = 12.5	1.3	16×10^{-4}	7.85	99×10^{-4}
$3\text{KIO}_4 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 3\text{KI} + 6\text{CO}_2 + 5\text{H}_2\text{O}$ (4.26)	230.0 (0.104)	162.14 (0.0370)	4:1	6.1	< 300	(14 / 3) = 4.67	(fuel is in excess)	1.8	23×10^{-4}	10.8	137×10^{-4}

Chemical model (stoichiometric oxidizer to fuel mass ratio)	Mol wt of SCO (moles of SCO)	Mol wt of fuel (moles of fuel)	Mass O:F ratio in 30-gram mix	Burn time, $\tau_{O:F}$ sec	SCO size - M&P, as shipped, or μm	Moles of gas produced per mole of oxidizer, $\left(\frac{\Delta n}{\alpha}\right)$	Moles of gas produced per mole of fuel, $\left(\frac{\Delta n}{\beta}\right)$	"Cold" gas volumetric production rate, Q_{298} liters/sec	Normalized "Cold" gas volumetric production rate, $\frac{Q_{298}}{V_{hood}}$ 1/sec	"Hot" gas volumetric production rate, Q_{1800} liters/sec	Normalized "Hot" gas volumetric production rate, $\frac{Q_{1800}}{V_{hood}}$ 1/sec
$6\text{Ca}(\text{ClO})_2 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow$ $6\text{CaCl}_2 + 5\text{H}_2\text{O} + 6\text{CO}_2$ (5.29)	143 (0.152)	162.14 (0.0370)	4:1	5.7	< 300	(17 / 6) = 2.83	(fuel is in excess)	1.7	22×10^{-4}	10.3	130×10^{-4}
$8\text{KMnO}_4 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow$ $8\text{MnO}_2 + 8\text{KOH} + 6\text{CO}_2 + \text{H}_2\text{O}$ (7.80)	158 (0.152)	162.14 (0.0370)	4:1	6.2	< 300	(23 / 8) = 2.88	(fuel is in excess)	1.6	20×10^{-4}	9.5	120×10^{-4}
$4\text{NaClO}_3 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow$ $4\text{NaCl} + 6\text{CO}_2 + 5\text{H}_2\text{O}$ (2.63)	106.5 (0.225)	162.14 (0.0370)	4:1	5.7	< 300	(oxidizer is in excess)	(15 / 1) = 15	2.4	29×10^{-4}	14.4	175×10^{-4}
$8\text{KNO}_2 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow$ $8\text{KOH} + 4\text{N}_2 + \text{H}_2\text{O} + 6\text{CO}_2$ (4.20)	85.11 (0.282)	162.14 (0.0370)	4:1	12.7	as shipped	(19 / 8) = 2.375	(fuel is in excess)	0.73	9×10^{-4}	4.4	56×10^{-4}

*****APPENDIX L:****Thermochemical Data for Heat Conduction Model**

**Table L-1.--Heats of formation at 1 atm. and 298° K for
reactants in SCO-fuel reactions**

Item	Chemical	Chemical Formula	Molecular Wt.	Heat of Formation kcal/gmol
1	Ammonium Nitrate	NH_4NO_3	80.05	-87.37
2	Ammonium Perchlorate	NH_4ClO_4	117.50	-70.58
3	Ammonium Persulfate	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	228.20	-393.9
4	Barium Chlorate	$\text{Ba}(\text{ClO}_3)_2$	304.27	-182.3
5	Barium Nitrate	$\text{Ba}(\text{NO}_3)_2$	261.35	-237.11
6	Calcium Hypochlorite	$\text{Ca}(\text{ClO})_2$	142.99	-162.1
7	Calcium Nitrate Tetrahydrate	$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	236.15	-509.64
8	Cellulose	$\text{C}_6\text{H}_{10}\text{O}_5$	162.14	¹ -230.8
9	Cerium Ammonium Nitrate	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$	548.23	² -504.7
10	Chromium Trioxide (g)	CrO_3	99.99	-70.00
11	Magnesium Perchlorate	$\text{Mg}(\text{ClO}_4)_2$	223.22	-135.97
12	Potassium Bromate	KBrO_3	167.01	-86.10
13	Potassium Chlorate	KClO_3	122.55	-95.06
14	Potassium Iodate	KIO_3	214.00	-119.83
15	Potassium Nitrate	KNO_3	101.11	-118.22
16	Potassium Nitrite	KNO_2	85.11	-88.39
17	Potassium Perchlorate	KClO_4	138.56	-103.43
18	Potassium Periodate	KIO_4	230.01	-111.67
19	Potassium Permanganate	KMnO_4	158.03	-200.1
20	Sodium Bromate	NaBrO_3	150.90	-79.85

Item	Chemical	Chemical Formula	Molecular Wt.	Heat of Formation kcal/gmol
21	Sodium Chlorate	NaClO ₃	106.45	-87.42
22	Sodium Chlorite	NaClO ₂	90.44	-73.38
23	Sodium Iodate	NaIO ₃	197.89	-115.15
24	Sodium Nitrate	NaNO ₃	85.01	-111.82
25	Sodium Nitrite	NaNO ₂	69.00	-85.72
26	Sodium Perchlorate Monohydrate	NaClO ₄ ·H ₂ O	140.46	-161.99
27	Sodium Periodate	NaIO ₄	213.89	-102.6
28	Sodium Peroxide	Na ₂ O ₂	77.99	-122.10

¹ Provided by Dr. Isaac A. Zlochower, PRL, NIOSH, CDC, based on data from Cheetah and TigerWin Software Libraries.

² Estimated by Dr. Isaac A. Zlochower, PRL, NIOSH, CDC.

**Table L-2.--Heats of formation at 1 atm. and 298° K
for products in SCO-fuel reactions**

Item	Chemical	Chemical Formula	Mole. Wt.	Heat of Formation kcal/ gmole	BP, °C
1	Ammonia (g)	NH ₃	17.03	-10.96	
2	Barium Chloride	Ba(Cl) ₂	208.25	-205.1	
3	Barium Hydroxide	Ba(OH) ₂	171.38	-226.1	
4	Calcium Carbonate	Ca(CO ₃) ₂	100.09	-288.46	
5	Calcium Chloride	CaCl ₂	110.99	-190.2	>1,600
6	Calcium Hydroxide	Ca(OH) ₂	74.09	-235.70	
7	Carbon Dioxide (g)	CO ₂	44.01	-94.05	
8	Carbon Monoxide (g)	CO	28.01	-26.416	
9	Dicerium Trioxide	Ce ₂ O ₃	328.24	-429.3	
10	Dichromium Trioxide	Cr ₂ O ₃	152.02	-271.2	
11	Dihydrogen Oxide (g)	H ₂ O	18.02	-57.796	
12	Dihydrogen Oxide (l)	H ₂ O	18.02	-68.315	100
13	Dipotassium Oxide	K ₂ O	94.19	-86.2	
14	Disodium Oxide	Na ₂ O	61.98	-99.00	At 1,950 a vapor pressure of one atm is achieved
15	Hydrogen Chloride	HCl	36.47	-22.063	
16	Magnesium Chloride	MgCl ₂	95.23	-153.35	1,412
17	Manganese Dioxide	MnO ₂	86.94	-124.29	

Item	Chemical	Chemical Formula	Mole. Wt.	Heat of Formation kcal/ gmole	BP, °C
18	Nitrogen	N ₂	28.01	0	
19	Potassium Bromide	KBr	119.01	-94.12	1,380
20	Potassium Carbonate	K ₂ CO ₃	138.20	-275.1	
21	Potassium Chloride	KCl	74.56	-104.38	1,500
22	Potassium Hydroxide	KOH	56.11	-101.52	1,320
23	Potassium Iodide	KI	166.02	-78.37	1,330
24	Sodium Bicarbonate	NaHCO ₃	84.01	-227.25	
25	Sodium Bromide	NaBr	102.91	-86.3	1,390
26	Sodium Carbonate	Na ₂ CO ₃	106.00	-270.26	
27	Sodium Chloride	NaCl	58.45	-98.26	1,413
28	Sodium Hydroxide	NaOH	40.01	-101.72	
29	Sodium Iodide	NaI	149.92	-68.78	1,300
30	Sulfur Dioxide (g)	SO ₂	64.07	-70.944	

Table L-3.—Heats of reaction at 1 atm. and 298° K
for oxygen-rich environments

Item	Reactants	→	¹ Products	¹ Heat of Reaction kcal
1	$12\text{NH}_4\text{NO}_3 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$12\text{N}_2 + 29\text{H}_2\text{O} + 6\text{CO}_2$	-961.14
2	$24\text{NH}_4\text{ClO}_4 + 5\text{C}_6\text{H}_{10}\text{O}_5$	→	$12\text{N}_2 + 61\text{H}_2\text{O} + 30\text{CO}_2 +$ 24HCl	-4,028.65
² 3	$4(\text{NH}_4)_2\text{S}_2\text{O}_8 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$8\text{NH}_3 + 9\text{H}_2\text{O}_{(l)} + 6\text{CO}_2 + 8\text{SO}_2$	-27.97
4	$2\text{Ba}(\text{ClO}_3)_2 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$2\text{BaCl}_2 + 5\text{H}_2\text{O} + 6\text{CO}_2$	-668.08
5	$12\text{Ba}(\text{NO}_3)_2 + 5\text{C}_6\text{H}_{10}\text{O}_5$	→	$12\text{Ba}(\text{OH})_2 + 13\text{H}_2\text{O} + 30\text{CO}_2$ $+ 12\text{N}_2$	-2,286.73
6	$6\text{Ca}(\text{ClO})_2 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$6\text{CaCl}_2 + 5\text{H}_2\text{O} + 6\text{CO}_2$	-791.08
7	$12\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} +$ $5\text{C}_6\text{H}_{10}\text{O}_5$	→	$12\text{Ca}(\text{OH})_2 + 61\text{H}_2\text{O} + 30\text{CO}_2$ $+ 12\text{N}_2$	-1,905.78
² 8	$24(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6 +$ $49\text{C}_6\text{H}_{10}\text{O}_5$	→	$192\text{NH}_3 + 53\text{H}_2\text{O} + 294\text{CO}_2 +$ $12\text{Ce}_2\text{O}_3$	-14,547.81
9	$8\text{CrO}_3 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$4\text{Cr}_2\text{O}_3 + 6\text{CO}_2 + 5\text{H}_2\text{O}$	-1,147.28
10	$3\text{Mg}(\text{ClO}_4)_2 + 2\text{C}_6\text{H}_{10}\text{O}_5$	→	$3\text{MgCl}_2 + 10\text{H}_2\text{O} + 12\text{CO}_2$	-1,297.10
11	$4\text{KBrO}_3 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$4\text{KBr} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	-654.56
12	$4\text{KClO}_3 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$4\text{KCl} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	-659.76
13	$4\text{KIO}_3 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$4\text{KI} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	-456.64
14A	$8\text{KNO}_3 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$4\text{K}_2\text{CO}_3 + 4\text{N}_2 + 5\text{H}_2\text{O} + 6\text{CO}_2$	-777.42
² 14B	$48\text{KNO}_3 + 10\text{C}_6\text{H}_{10}\text{O}_5$	→	$48\text{KOH} + 24\text{N}_2 + 26\text{H}_2\text{O} +$ 60CO_2	-4,036.10
² 15	$8\text{KNO}_2 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$8\text{KOH} + 4\text{N}_2 + \text{H}_2\text{O} + 6\text{CO}_2$	-496.34
16	$3\text{KClO}_4 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$3\text{KCl} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	-625.33
17	$3\text{KIO}_4 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$3\text{KI} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	-522.58
³ 18	$8\text{KMnO}_4 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$8\text{MnO}_2 + 8\text{KOH} + 6\text{CO}_2 + \text{H}_2\text{O}$	-596.98
19	$4\text{NaBrO}_3 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$4\text{NaBr} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	-648.28
20	$4\text{NaClO}_3 + \text{C}_6\text{H}_{10}\text{O}_5$	→	$4\text{NaCl} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	-665.84

21	$6\text{NaClO}_2 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 6\text{NaCl} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	-771.76
22	$4\text{NaIO}_3 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 4\text{NaI} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	-437.00
23A	$8\text{NaNO}_3 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 4\text{Na}_2\text{CO}_3 + 4\text{N}_2 + 5\text{H}_2\text{O} + 6\text{CO}_2$	-808.96
23B	$48\text{NaNO}_3 + 10\text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 48\text{NaOH} + 24\text{N}_2 + 26\text{H}_2\text{O} + 60\text{CO}_2$	-4,352.90
² 24	$8\text{NaNO}_2 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 8\text{NaOH} + 4\text{N}_2 + \text{H}_2\text{O} + 6\text{CO}_2$	-519.30
25	$3\text{NaClO}_4 \cdot \text{H}_2\text{O} + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 3\text{NaCl} + 6\text{CO}_2 + 8\text{H}_2\text{O}$	-604.68
26	$3\text{NaIO}_4 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 3\text{NaI} + 6\text{CO}_2 + 5\text{H}_2\text{O}$	-521.02
⁴ 27A	$12\text{Na}_2\text{O}_2 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 6\text{Na}_2\text{CO}_3 + 10\text{NaOH} + \text{Na}_2\text{O}$	-1,041.76
27B	$12\text{Na}_2\text{O}_2 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 7\text{Na}_2\text{O} + 6\text{CO}_2 + 10\text{NaOH}$	-578.50
27C	$12\text{Na}_2\text{O}_2 + \text{C}_6\text{H}_{10}\text{O}_5 \rightarrow 6\text{NaHCO}_3 + 4\text{NaOH} + 7\text{Na}_2\text{O}$	-767.38

¹ Water in the products is in the gaseous phase except when noted otherwise.

² These products were suggested by Dr. Isaac A. Zlochower, PRL, NIOSH, CDC.

³ This reaction assumes MnO_2 is main oxide formed.

⁴ This reaction assumes following reaction also occurs.



***GLOSSARY

ALTERNATIVE REFERENCE STANDARDS: proposed noncarcinogenic SCO reference standards to be mixed with either cellulose or sawdust of sufficient fineness in appropriate mass ratios to give "best" possible agreement with the published US and UN Packing Group classification numbers for a large collection of SCOs.

"BEST" ESTIMATE OF STANDARD DEVIATION OF POPULATION: a statistical estimate of the standard deviation for the parent population which is obtained from a prescribed procedure that is often derived by use of the "Fisher Maximum Likelihood Estimator" method.

BURN TIME FOR UN TEST: time for combustion process based on difference in times between cessation of combustion and first application of heat to the mixture with the heating power to the wire being applied throughout the combustion process.

BURN TIME FOR US TEST: time for combustion process based on difference in times between cessation of combustion and first observable onset of combustion with the heating power turned off shortly after the onset of combustion.

BURNING: in common usage it is defined as a *combustion* in which the material is consumed by fire resulting from interaction of the material with atmospheric oxygen at high temperature and accompanied by flame and sometimes sound.

CARCINOGEN: chemical species or agent known to cause cancer in animals and/or humans, such as potassium bromate, a human carcinogen by the State of California and suspected human carcinogen by the IARC. [REFERENCE SOURCES: (IR 1, 4, 6, and 7)]

COMBUSTION: to most people combustion implies the process of *burning* and is generally associated with *flaming*. Most people perceive that combustion is due to the combination of a combustible substance with atmospheric oxygen and the consequent evolution of heat. The appearance of flame is due to the oxidation of gases or vapors at a very rapid rate, producing sufficiently high temperatures to cause the molecules involved to be radiant. However, the term *combustion* has a broader meaning and is extended to other forms of oxidation. Strictly speaking, the combustion

of a mixture may take place in the absence of atmospheric oxygen. Broadly speaking, **combustion** is a chemical reaction process involving oxidizing and reducing agents that generates much heat and high temperatures. In **rapid oxidation** very high temperatures due to intense heat are attained and, usually, light is given off. In **slow oxidation**, the process is not accompanied by high temperature and light. Combustion must be distinguished from **deflagration, explosion, and detonation** which involve very rapid combustion processes; detonation involves extremely rapid shock propagation. An explosion or detonation is often accompanied by a thundering noise. At normal atmospheric temperatures oxidation for most materials occurs only very slowly and usually with little outward manifestation if at all. When, however, the temperature is raised sufficiently, the process becomes greatly accelerated. When the **ignition point** is reached, heat will be developed at a rate greater than that at which it can be dissipated and flaming can ensue. In some situations with atmospheric oxygen participating, the heat generated will volatilize solid or liquid components in a mixture and the combustion process will proceed rapidly in the gas phase (deflagration). The combustion of SCO-fuel mixtures does not require atmospheric oxygen. Once ignition occurs the reaction can proceed very rapidly and sometimes violently.

Note : If explosives or propellents are spread out on the ground and ignited from one end, the rate of burning is often a few mm to a few cm per second. It is higher for confined substances and sometimes develops into deflagration, explosion, or detonation. [SOURCE: (PR 22): Basil T. Fedoroff and Oliver E. Sheffield, Encyclopedia of Explosives and Related Items, PATR 2700, Volume 4, Picatinny Arsenal, Dover, New Jersey, 1969, pages D217.]

CONFIDENCE INTERVAL: in statistics, the interval bounded by confidence limits. [REFERENCE

SOURCE: Keeping's textbook (PR 16)]

CONFIDENCE LIMITS: in statistics, a pair of numbers used to estimate a characteristic of a population, such that the numbers can be stated with a specified probability that the population characteristic is included between them. [SOURCE: Keeping's textbook (PR 16)]

DEFLAGRATION IN EXPLOSIVES: a chemical reaction process in which the zone of the burning moves suddenly and violently but at a velocity less than the speed of sound in the unreacted material. Deflagrating explosives are substance which upon being heated (such as between temperatures of 500 to 1700 ° C (or subjected to flame, sparks, shock, friction, etc.), while unconfined and in small quantities, ignite suddenly and burn much quicker than in ordinary combustion. The burning of deflagrating explosives usually proceeds rather violently and is accompanied by a flame (or sparks) and a hissing (or crackling) sound, but not with a sharp loud report as in the case of *detonating explosives*. **Deflagration in explosives** is a mode of explosion distinguished from detonation and constituting the very rapid autocombustion of particles of explosive as a surface phenomenon. In the case of deflagration, the reaction products flow away from the unreacted material, while in detonation these are at extremely high pressure and flow toward the unreacted material. On initiation of deflagration, local finite "hot spots" are developed either through friction between the grains, or by adiabatic compression of gases in interstices between the grains and in bubbles within liquids. In either case, heterogeneous decomposition of the material at the grain or bubble surface produces heat and volatile intermediates. These products undergo highly exothermic reactions in the gas phase; and the additional heat is more than sufficient to cause decomposition and volatilization from the newly exposed surface. This means that deflagration is self-propagating. If an explosive is finely divided (unconfined or semi-confined) and is in the form of a large mass, then deflagration can occur simultaneously throughout the mass. In such case, the partial confinement of the particles within the mass, because of the viscosity of gaseous products, has the effect of increasing pressure, and this in turn, causes an increase in the rate of deflagration and in the temperature. The final result of increase in pressure of unconfined explosives might be violent deflagration, but no detonation, except when very large quantities are present as those stored in powder magazines. **If, however, the explosive is under confinement, the deflagration might undergo transition into explosion or detonation.** Confinement permits rapid increase in

pressures with a consequent rapid increase in the rate of deflagration. If the rate reaches the value of 1,000 meters/second, it is no longer deflagration, but rather *low-order detonation*.

The velocity of the reaction wave in a deflagration is between that of 'combustion' and low-order detonation. (It is fairly well accepted that for a deflagration that the maximum velocity is of the order of 1,000 meters/second.) If the rate increases to 5,000 meters/second, the reaction process is clearly *high-order* detonation. The transition of deflagration into detonation is "almost discontinuous." Some contend that it is caused by shockwaves formed within the mass of the explosive by the hot product gases from the surface undergoing very rapid deflagration.

Note: The above exposition on deflagration is based extensively on the work of Basil Fedoroff and Oliver Sheffield. [SOURCE (PR 22): Basil T. Fedoroff and Oliver E. Sheffield, Encyclopedia of Explosives and Related Items, PATR 2700, Volume 3, pages D38-39, and Volume 4, page D217, Picatinny Arsenal, Dover, New Jersey, 1969.]

DELIQUESCENT: to become liquid by a solid absorbing moisture from the air.

DETONATION: "an exothermic chemical reaction that propagates with such rapidity that the rate of advance of the reaction zone into the unreacted material exceeds the velocity of sound in the unreacted material, that is the advancing reaction zone is associated with a *shock wave*. The rate of advance of the reaction zone is termed *detonation rate* or *detonation velocity*. When this rate of advance attains such a value that it will continue without diminuation through the unreacted material, it is termed a *stable detonation velocity*." "When the detonation rate is equal to or greater than the stable detonation velocity of the explosive, the reaction is termed a *high-order detonation*. When the detonation rate is lower than the stable detonation velocity of the explosive, the reaction is termed a *low-order detonation*. [SOURCE (PR 22): Basil T. Fedoroff and Oliver E. Sheffield, Encyclopedia of Explosives and Related Items, PATR 2700, Volume 4, Picatinny Arsenal, Dover, New Jersey, 1969, pages D217-218.]

Note: The theory of detonation for gases and condensed phase matter is important, is directly relevant to solid oxidizers, and has attracted the attention of many scientists. There is a

tendency for this subject to be infrequently addressed in the "open" American literature. Fortunately, the Russian classic, Theory of Detonation, written (PR 23) by Professors Ia. B. Zel'dovich and A. S. Kompaneets in 1955, was translated into English and published by Academic Press in 1960. This book is well-written and easy to understand; it was written for students by two famous Russian scientists. The Academy of Sciences of the USSR Press, in 1946 published (PR 24) in Russian another important book by Zel'dovich entitled, Theory of Shock Waves and Introduction to Gas Dynamics. These two useful books go "hand-in-hand" in understanding the theory of detonation. Whether this latter textbook was translated into English and published in the "open" literature is uncertain.

DISTRIBUTION FUNCTION: a function of any random variable that assigns to each number the probability that the random variable takes a value less than or equal to the given number. There are two basic types - discrete and continuous. For the continuous case, we have

for a given number x , this probability being $\int_{-\infty}^x p(t)dt$, where $p(t)$ is the probability density

function. [SOURCE: Keeping's textbook (PR 16)]

EXPLOSIVE: (for the Legal US definition of explosive consult § 173.50 Class 1 - definitions of 49 CFR Part 100-177, Chapter 1) in approximate terminology, an **EXPLOSIVE** means any substance or article, including a device, which is designed to function by explosion (i.e., an extremely rapid release of gas and heat) or which, by chemical reaction within itself, is able to function in a similar manner even if not designed to function by explosion. Explosives in Class 1 are divided into six divisions as follows:

(1) **Division 1.1** consists of explosives that have a mass explosion hazard. A mass explosion is one that affects almost the entire load instantaneously.

(2) **Division 1.2** consists of explosives that have a projection hazard but not a mass

explosion hazard.

(3) **Division 1.3** consists of explosives that have a fire hazard and either a minor blast hazard or a minor projection hazard or both, but not a mass explosion hazard.

(4) **Division 1.4** consists of explosives that present a minor explosion hazard. The explosive effects are largely confined to the package and no projection of fragments of appreciable size or range is to be expected. An external fire must not cause virtually instantaneous explosion of almost the entire contents of the package.

(5) **Division 1.5** consists of very insensitive explosives. This division is comprised of substances which have a mass explosion hazard but are so insensitive that there is very little probability of initiation or of transition from burning to detonation under normal conditions of transport. (The probability of transition from burning to detonation is greater when large quantities are transported in a vessel.)

(6) **Division 1.6** consists of extremely insensitive articles which do not have a mass explosion hazard. This division is comprised of articles which contain only extremely insensitive detonating substances and which demonstrate a negligible probability of accidental initiation or propagation. (The risk from articles is limited to the explosion of a single article.)

Note 1: According to CFR § 172.102 when ammonium perchlorate has a particle size < 45µm, it falls into the Division 1.1 explosives category.

Note 2: According to the UN Manual of Tests and Criteria, 2nd revised edition (PR 2), when ammonium perchlorate of 45 µm size is subjected to the *Internal Ignition Test* in a 45-mm diameter “pipe”, it causes destruction of the vessel, indicating the substance undergoes transition from deflagration to detonation (see page 45).

Note 3: Thus, care is needed in the grinding of some SCOs - otherwise they may be turned into

explosives.

EXTREME: statistical term denoting a measurement value that is less than or greater than most of the values clustered about the mean (see outlier).

F-DISTRIBUTION: a statistical distribution used in characterizing parameters (often the standard deviation) associated with small sample sizes. [SOURCE: Keeping's textbook, Introduction to Statistical Inference (PR 16)]

HUMAN CARCINOGEN: chemical species or agent known to cause cancer in humans, such as chromium trioxide. [SOURCES: (IR 1, 4, 6, and 7)]

HYGROSCOPIC: absorbing or attracting moisture from the air.

HYPOTHESIS TESTING: a formal statistical procedure to test hypotheses often about measurements based on the use of probability distributions, number of measurements in a sample set, and acceptable levels of error (covered in the discipline of statistical inference testing). Hypothesis testing is useful in comparing measurements to see if they are the same or different or whether they are less than or greater than a set value when there is scatter in the data. It takes into account the number of measurements involved in each set that is being compared. [SOURCE: Keeping's textbook, Introduction to Statistical Inference (PR 16)]

INTERVAL ESTIMATION: in statistics the process of estimating a parameter of a given population by specifying an interval of values and the probability that the true value of the parameter falls within this interval. [SOURCE: Keeping's textbook, Introduction to Statistical Inference (PR 16)]

LEVEL OF SIGNIFICANCE (α): in statistics it is the value of a level acceptability (sometimes error) in hypothesis testing. [SOURCE: Keeping's textbook, Introduction to Statistical Inference (PR 16)]

LIQUID CHEMICAL OXIDIZER (LCO): chemical species in liquid state that is capable of undergoing a combustion type reaction with a fuel (either a solid or a liquid).

LOG NORMAL DISTRIBUTION: a non symmetric probability distribution function that is often used to characterize the particle size of a SCO. It is distribution of a random variable for which the logarithm of the variable has a normal distribution. [SOURCE: Keeping's textbook (PR 16)]

MEAN OF SAMPLE: statistical term denoting arithmetic average of sample of size n . Symbolically, the

mean $\bar{t}$ is given by $\left(\frac{1}{n}\right) \sum_{i=1}^n t_i$. This formula was used to obtain the mean burn time.

MEAN OF PARENT POPULATION: statistical term denoting arithmetic average for a large population from which a sample is extracted - sometimes the population is considered to have an infinite number of values.

NORMAL DISTRIBUTION: a symmetric bell-shaped probability distribution function, also called a Gaussian distribution. It is the principal distribution in statistics to which the other distributions of sample means approach in the limiting sense, as the number of the elements in the sample approaches infinity. [SOURCE: Keeping's textbook (PR 16)]

OUTLIER: statistical term denoting a measurement that is located far from or outside the main group of values that is clustered around the mean. [SOURCES: Keeping's textbook, Introduction to Statistical Inference, (PR 16) and Gumbel's book, Statistics of Extremes, (PR 21)]

PACKING GROUP: hazard classification (category) number - the lower the group number, the more hazard is. [SOURCES: (PR 1, 2, and 3)]

PARENT POPULATION: collection of measurements or variates that comprises a universal set of numbers from which a finite sample can be extracted.

POINT ESTIMATION: in statistics the process of determining a single estimated value of a parameter of a given population.

PROBABILITY: the relative possibility that an event will occur, as often expressed by the ratio of the number of actual occurrences to the total number of possible occurrences. It is the relative frequency with which an event occurs or is likely to occur.

PROBABILITY DENSITY FUNCTION (pdf): in the continuous case, it is a function, $p(t)$, of a

continuous variable, t , whose integral, $\int_a^b p(t)dt$, over a region gives the probability that a

random variable falls within the region, $[a,b]$. In the discrete case, it is a function of a discrete variable whose sum over a discrete set gives the probability of occurrence of a specified value. The pdf is also known as a frequency function. [SOURCE: Keeping's textbook (PR 16)]

RECYCLING OF POLLUTANTS: unscrubbed pollutants from an exhaust hood being emitted to the atmosphere and carried back into laboratories by natural air currents. In some situations sulfur dioxide produced in reacting ammonium persulfate with either cellulose or sawdust (a reaction that can continue for at least 8 minutes), can be recycled into the test laboratory, creating an occupational health problem.

REFERENCE STANDARDS FOR UN TEST PROTOCOL: burn times in seconds for 30-gram mixtures of potassium bromate-cellulose in 3:7, 2:3, and 3:2 mass ratios of oxidant to fuel made with bromate of particle size cut from 150 to 300 μm . [SOURCE: UN Manual of Tests and Criteria (PR 2)]

REFERENCE STANDARDS FOR US TEST PROTOCOL: burn times in seconds for three 30-gram mixtures of SCO-softwood sawdust in 1:1 mass ratios of oxidant to fuel with the SCO's being ammonium persulfate, potassium perchlorate, and potassium bromate made with the SCO having a particle size of $< 300 \mu\text{m}$ and the sawdust being less than 1,600 μm . [SOURCE: U. S. Code of Federal Regulations (PR 3)]

SAMPLE POPULATION: collection of measurements or variates in a sample from a parent, very large or universe collection of values.

SAMPLE SIZE: number of measurements in a sample.

SASH: window that blocks air into or out of a chemical exhaust hood.

SASH OPENING: the area under the sash and above the working base of the exhaust hood through which gases and particulates can travel into and out of the hood. If the hood is overwhelmed by a

violent reaction performed in the hood, the products and entrained reactants can jet out through the sash opening into the work area.

SCRUBBING SYSTEM: cleaning system mentioned (PR 2) in the UN Test procedure that is on exhaust side of hood to collect, trap, and neutralize gaseous and particulate pollutants and prevent them from entering the air environment. The use of a scrubbing system would eliminate problems in some laboratory situations caused by reacting ammonium persulfate.

SOLID CHEMICAL OXIDIZER (SCO): chemical species in a solid state that is capable of undergoing a combustion type reaction with a fuel (either a solid or a liquid).

STRAGGLER: statistical term denoting a measurement value that is less than most of the values clustered about the mean (see outlier).

STANDARD DEVIATION OF SAMPLE: statistical measure of how the sample measurement are clustered about the sample mean, $\bar{t}$. It is a measure of dispersion in a frequency distribution, equal to the square root of the mean of the squares of the deviations from the arithmetic mean of the distribution. In terms of the variate time, t , the standard deviation, s , is given by

$$s = \sqrt{\left(\frac{1}{n} \sum_{i=1}^n (t_i - \bar{t})^2 \right)}.$$

STANDARD DEVIATION OF PARENT POPULATION: statistical measure of how the measurements from the parent population (sometimes of infinite sample size) are clustered about the parent population's mean. Symbolically, the calculation of the estimated standard deviation σ of the parent population is obtained from

$$\sigma = \sqrt{\left(\frac{1}{n-1} \sum_{i=1}^n (t_i - \bar{t})^2 \right)}.$$

In the obtaining the standard deviation for the mean

burn time, t , of the SCO this formula was used.

t-DISTRIBUTION: statistical distribution used in characterizing parameters (often the mean) associated with small sample sizes. It is a bell-shaped probability distribution that is flatter or more stretched out than the normal distribution. It is also known as **student's t-distribution**. [SOURCE: Keeping's textbook, Introduction to Statistical Inference (PR 16)]

VARIANCE OF SAMPLE VARIATE: a statistical term that has as its value the square of the standard deviation of the sample.

VARIANCE OF A PARENT POPULATION VARIATE: a statistical term that has as its value the square of the variate's parent population standard deviation.

WASH DOWN HOOD: chemical exhaust hood having an integral cup type drain sink to collect water from washing down the hood's internal surfaces using sprays from fixed and variable locations for use in testing SCOs. It should have water faucets. When corrosive materials are to be used in the hood, the internal surfaces of the hood should be made from corrosive resistant material such as type 316 stainless steel. The hood for handling SCOs similar in reactivity to perchloric acid is known as a perchloric acid hood. Because some of the SCOs are extremely toxic, such as soluble barium type oxidizers, etc., a collecting tank can be fastened to the drain to avoid dumping "difficult" materials into the sewer. Such a hood should be equipped with a bottom airfoil, below the sash. [SOURCE: DOI's Employees Accident Prevention Handbook (PR 14)]

A sufficiently large wash down hood would greatly help to reduce laboratory contamination and enable studies with the more "difficult" SCOs to be conducted in a safer manner. It would be especially useful in the pulverization of large quantities of SCOs such as could be done with the Retsch mill. Although a large wash down hood is expensive, when working with the more "difficult" SCOs and dangerous goods, having one available would be prudent and would significantly enhance the level of occupational health and safety in the research environment. A scrubber system on the hood would greatly minimize recycling of pollutants into the work area. They would also be of value to laboratories conducting compliance tests on SCOs and LCOs.

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE 14 Mar 1998	3. REPORT TYPE AND DATES COVERED 28 April 1995	
4. TITLE AND SUBTITLE EVALUATION OF US AND UN TEST PROCEDURES FOR DETERMINING SHIPPING HAZARDS OF SOLID OXIDIZERS			5. FUNDING NUMBERS
6. AUTHOR(S) Nevin B. Greninger, Gene F. Friel, and Thomas C. Ruhe			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) NIOSH, Pittsburgh Research Laboratory, P.O. Box 18070, Cochrans Mill Road Pittsburgh, PA 15236			8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) US Department of Transportation (DOT), Research and Special Programs Administration, Office of Hazardous Materials Technology, DHM-21, 400 Seventh St., S. W., Washington, DC, 20590-0001			10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES The research was funded under Interagency Agreement DTRS56-95-X-0029, entitled "Evaluation of New UN Test Methods for Classification of Solid and Liquid Oxidizers."			
12A. DISTRIBUTION/AVAILABILITY STATEMENT Available to the public			12B. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) An evaluation study of UN and US test procedures for solid chemical oxidizers (SCOs) was performed by the National Institute for Occupational Safety and Health (NIOSH) for the US Department of Transportation (DOT). Eighteen solid oxidizers were mixed with cellulose (UN test) and fourteen with sawdust (US test). Burning times were compared with those from reference mixtures. Twenty-nine percent of the UN published hazard classifications were confirmed using potassium bromate (KBrO ₃) with a particle size from 150 to 300 µm. For sizes of this carcinogen less than 150 µm, 71% were confirmed. In tests with the proposed noncarcinogenic potassium chlorate (KClO ₃) reference less than 300 µm in size, 76 % of the classifications were confirmed. Classifications that were based on the US protocol, using three different reference chemicals specified were confirmed for 21 % of the cases. The data provides a basis for adopting a modified version of the UN protocol featuring the replacement of the bromate standard with potassium chlorate. If it is decided to retain the US protocol, then similar changes are recommended. There would be then only minor differences between the US and UN protocols. Proposed future work is discussed, including modeling, information retrieval, particle size effect on burn time, and the reactivity of liquid oxidizers in open and semi-confined environments. Approximately 800 combustion tests were conducted.			
14. SUBJECT TERMS Solid Oxidizers, Test Procedures for US & UN, Shipping Hazard Evaluation			15. NUMBER OF PAGES 252
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR

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