Organic Fuels: Composition and Formation Enthalpy Part II — Resins, Charcoal, Pitch, Gilsonite, and Waxes

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ABSTRACT

The utilization of free energy minimization computer programs in areas of combustion research is likely to increase in the future. These programs require the specification of the reactant chemical formulas and their respective formation enthalpies as part of the input data set. Frequently, for common compounds, the values required are readily available in handbooks. Complex organic compounds or poorly characterized mixtures may not have the required data available in a directly usable form. This article evaluates a variety of organic fuels used in pyrotechnics from the perspective of establishing useful chemical formulas and formation enthalpies. Along the way, it is the author's intention to simplify the methods used, to illustrate how many disparate sources of information may be drawn upon to achieve the estimation of the required values, and to demonstrate that each of the methods used is itself relatively easy to perform or calculate.

Keywords: chemical composition, enthalpy of formation, higher heating value (HHV), Benson Group, free energy minimization, ultimate analysis, trace elements, acaroid resin, Xanthorrhoea, shellac, charcoal, pitch, gilsonite, bitumen, wax, paraffin, beeswax, naphthalene, anthracene, hexachlorobenzene, gallic acid, polyvinyl chloride, polyvinylidene chloride, hexamethylenetetramine, sodium benzoate, sodium salicylate, stearin

Introduction

A considerable variety of organic fuels are available for, and used in, pyrotechnic formulations. Choosing the right fuel for the intended application is made all the more difficult if the data required to make an informed decision is incomplete or unavailable. The primary focus of this article is to present chemical formulas and formation enthalpy estimates for common organic fuels that will be useful to the pyrotechnist and energetics chemist.

The author believes that, in the future, the use of *free energy minimization* software will find wider acceptance as an important tool for use in the combustion products analysis of pyrotechnic formulations. These programs allow the investigator to simulate, study, and optimize the combustion properties of a pyrotechnic formulation prior to actually handling the potential ingredients. This will certainly expedite the formulation development cycle and improve the end product.

These programs require, in part, that the chemical composition and formation enthalpies of the ingredients—the *reactants*—be specified as part of the input data set. The compositions of these fuels range from simple, pure compounds to complex mixtures that are poorly characterized. Many of the fuels have variable composition, and this may be due in part to the source location, climate, collection time of year, or species. In some cases, the chemical compositions are readily available in handbooks. The formation enthalpies, on the other hand, are rarely available, but may be estimated using a variety of methods.

The reference values listed in the following tables are expressed as either *higher heating* value (HHV), formation enthalpy ($\Delta_{\rm f}$ H°), or

combustion enthalpy ($\Delta_c H^\circ$). Units of kilojoule (kJ) or megajoule (MJ) per kilogram (kg) or mole are used for both. Formation enthalpies are for the solid phase unless otherwise indicated. The method used for estimating the $\Delta_f H^\circ$ is denoted by superscripted letters following the value:

Н	HHV's
С	Combustion Enthalpy
В	Benson Group Additivity
PB	Partial Benson Group Additivity
Е	Equation
F	Flame temperature and formulation

Each of these methods is described in "Six Methods for Estimating the Formation Enthalpy of Organic Compounds".^[1] For convenience, the chemical formulas are generally represented using a common basis such that comparisons may be readily made between the different fuels. The author arbitrarily chose a C_6 formula basis because many fuels are derived from simple C_6 -based molecules. CAS numbers are provided when available.

Part One^[2] covered organic fuels based on wood, its direct derivatives, related carbohydrates, exudates, and rosin.

Part Two covers acaroid resin, shellac, the destructive distillation of wood: charcoal and pitch, Gilsonite, waxes, and a sampling of pure fuels and synthetic polymers.

Acaroid Resin

Acaroid resin (sometimes spelled *Accroides*) is derived from the Australian "grass tree" *Xan*-*thorrhoea* (also known as *yacca*,^[3] or *blackboy* due to the blackened trunks burned by bush fires^[3–5]). The resin exudes from the plant and cements the bases of the dead leaves together and so forms the bulk of the trunk.^[3,5,6] It is remarkable for its high phenolic content.^[6] The fresh resin obtained is known as *Yacca gum*^[7] and is chemically simpler than the aged resin.^[4] Resins that have been partially pyrolized by bush

fires are the acaroid resins,^[7] and fall into two principal categories that differ markedly:^[6]

- *Yellow acaroid,* also known as *Botany Bay gum*,^[8] is produced by *X. hastilis*^[3,4] ("*Spear Grass Tree*"^[5]), and is relatively rare.
- *Red acaroid*, also known as *Grass Tree gum*, *Blackboy gum*,^[8] and *Red Gum*^[9] is produced by *X. australis*^[3] ("*Austral Grass Tree*"^[5]), *X. preissii*,^[3,10] *X. arborea*^[3] ("*Great Resin Grass Tree*" or "*Dackowar*"^[5]), *X. reflexa*,^[11] and other *Xanthorrhoea* species.^[3]

There are 28 species in the genus *Xanthor*rhoea,^[12] and there seems to be general confusion in their individual identification^[6,13] and from which species analytical samples originated.^[6,10,13] An early report^[10] attributed the yellow resin to *X. tateana*, but a more recent report^[3] indicates that a red resin is produced instead. *X. australis*, on the other hand, produces a brittle red resin, and also a sticky yellow resin present at the leaf bases.^[6] The presence of both color resins may be due, in part, to aging and natural oxidation.^[3]

Unfortunately, there is no one, complete, composition for any of the resins. To make matters worse, each incomplete description differs significantly from the others. The experiment descriptions sometimes include vague values regarding the initial weight of resin extracted from the raw samples, or the amounts soluble in various solvents, etc. Estimates of the chemical composition and $\Delta_f H^o$ will be made, but the reader is cautioned to weigh these tentative estimates accordingly.

Early work^[10,11] focused on the analysis of the *essential oils*, which constitute a small fraction of the total resin. See Table 1.

Later work focused on clarifying or correcting earlier works^[13,14] and identifying specific *flavonoids* present in the resins.^[4,6,15] Very little analytical work has been done, and the compositions of the bulk of the resins remains largely unknown.^[5,6,15,16]

	X. arborea	X. hastilis	X. reflexa
Percent of resin	1.0 (approx.)	1.56	6.86
Component:			
Primary	Pæonol 50%	Cinnamyl alcohol 53%	Pæonol 62.8%
Secondary	—	—	Xanthorrhoein 17.5%
C ₆ basis formula	C ₆ H _{6.67} O ₂	C ₆ H _{6.67} O _{0.67}	C ₆ H _{6.47} O _{1.65}
$\Delta_{\rm f} {\rm H}^{\rm o}$ (kJ/mole _{liquid} ^B)	-513.3	-107.0	-460.4
Structure	OH OH	OH	OCH3
	Pæonol 89-84-9	Cinnamyl alcohol 104-54-1	Xanthorrhoein

Table 1. Principle Components of Essential Oils from Xanthorrhoea.^[a]

Note: Xanthorrhoein –270.3, Pæonol –513.3, Cinnamyl alcohol –107.0, $\Delta_f H^o kJ/mole_{liquid}^B$

[a] Components and percentages from reference 11.

Alcohols very closely related to coniferyl alcohol—see Figure 1—were shown to be present in the red acaroid resin.^[17] The terms *resinotannol*,^[3,10] *erythroresinotannol* ($C_{40}H_{40}O_{10}$),^[8] or *xanthoresinotannol* ($C_{43}H_{46}O_{10}$)^[8] were occasionally used as generic names for the alcoholic constituents that may be present in the resin, and which formed an ester with either p-*coumaric* or *cinnamic acid*.^[8] See Figure 1. A more recent report uses the term *benzoresinotannol*.^[7]

Resinotannols are related to *tannins*.^[3] A partial definition of a vegetable tannin is a wa-

ter-soluble phenolic compound having a molecular weight between 500 and 3000.^[18] Condensed tannins are polymers derived from *fla*vonoid monomers, and are very susceptible to polymerization by influence of heat.^[19] This may account for part of the complexity of these resins, as bush fires frequent the localities of many of the grass tree species. Examples of flavonoids are the *flavan*, 4',5,7-trimethoxyflavan, and the *flavanones*, *hesperetin* and *pinocembrin*. See Figure 2. Condensed tannins are the most widespread and commercially significant plant phenolics; however, their chemistry is still

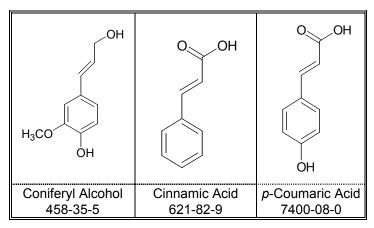


Figure 1. Coniferyl alcohol and closely related compounds.

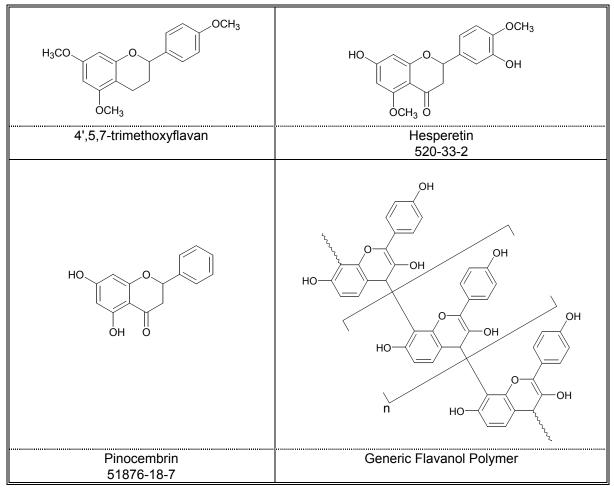


Figure 2. Examples of flavanoids.

undeveloped.^[18,20] Along with condensed tannins are found complex phenolic substances that are ill-defined.^[19] An example of a generalized structure of a polymeric *flavanol* is depicted in Figure 2. If this arbitrary flavanol formed an ester with *p*-coumaric acid, the resulting hypothetical resinotannol would have a C₆ formula of C₆H₄O_{1.5}, Δ_f H^o –192 kJ/mole^B.

A recent report provides ultimate analysis data for resins of *X. preissii*, *X. reflexa*, and yacca gum, and also $\Delta_f H^\circ$ data for each in units of kJ/mole.^[7] Unfortunately, chemical formulas

or molecular weights were not provided in the report^[7] or by the report's author;^[21] thus there is no way to reconcile the molar-based $\Delta_f H^{\circ}$ values to the mass-based ultimate analysis data. Nevertheless, a representative chemical formula derived from the average of the ultimate analysis values for red acaroid resins is C₆H_{5.95}O_{2.63}N_{0.01}, and for yacca gum C₆H_{6.78}O_{3.09}N_{0.05}. The yacca gum oxygen and hydrogen both decrease, apparently as a result of the loss of volatiles^[7] and hydroxyls^[21] due to bush fire pyrolysis, when transformed into red acaroid resin.

Compound	X. hastilis	X. australis	Formula	$\Delta_{\rm f} {\rm H^o}$, kJ/mole
cinnamyl p-coumarate	50		$C_{18}H_{16}O_{3}$	-402.9 ^B
p-coumaric acid	4.17	35	C ₉ H ₈ O ₃	-529.69 ^[a]
methyl cinnamate	3.33		C ₁₀ H ₁₀ O	–290.79 ^[a]
hesperetin	1.35		$C_{17}H_{16}O_{6}$	–992.57 ⁸
cinnamic acid	0.83	9	C ₉ H ₈ O ₂	-337.23 ^[b]
cinnamyl alcohol	0.67		C ₉ H ₁₀ O	–131.3 ⁸
cinnamyl cinnamate	[C]		$C_{18}H_{16}O_2$	–198.1 ⁸
chrysophanic acid	[C]		$C_{15}H_{10}O_4$	–596.1 ⁸
xanthorrhoeol		12 ^[d]	$C_{15}H_{14}O_{3}$	–545.8 ⁸
Percentage	60.35	56		
Formula	C ₆ H _{5.59} O _{1.15}	C ₆ H _{5.42} O _{1.66}		
∆ _f H ^o kJ/mole ^{B,R}	-414.8	-502.2		

Table 2. Constituents of Xanthorrhoea Resins.

Note: all $\Delta_f H^o$ values for the solid phase. Percentages from reference 6.

- [a] $\Delta_f H^o$ data from reference 23.
- [b] $\Delta_f H^o$ data from reference 24.
- [c] Present, but no percentages given.
- [d] At least 12 percent is present.

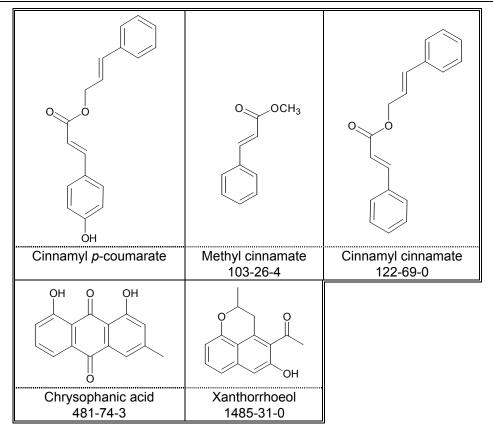


Figure 3. Some constituents of Xanthorrhoea resin.

Table 3. $\Delta_f H^\circ$ Values for Some Acaroid Resins.

Resin	C ₆ -Basis Formula	$\Delta_{\rm f} {\rm H}^{\rm o} \ ({\rm kJ/mol})^{[a]}$
Erythroresinotannol	$C_{6}H_{6}O_{1.5}$	–260 ^E
Xanthoresinotannol	C ₆ H _{6.419} O _{1.395}	–255 ^E
<i>p</i> -coumaric ester	C ₆ H _{6.115} O _{1.5}	–263 ^E
X. hastilis (60.35%)	C ₆ H _{5.59} O _{1.15}	–414.8 ⁸ , ref
X. australis (56%)	C ₆ H _{5.42} O _{1.66}	–502.2 ⁸ , ref.
Red acaroid	C ₆ H _{5.95} O _{2.63} N _{0.01}	-470 ^{E [b]}
Yacca gum	$C_6H_{6.78}O_{3.09}N_{0.05}$	–594 ^{E [b]}

[a] Equation 5 used from reference 1.

[b] The nitrogen present is sufficiently small to ignore and allow a tentative estimate to be made using equation 5 from reference 1.

One reference^[22] lists a composition for both red and yellow acaroid resin as 85% *p*-coumaric ester of xanthoresinotannol. An approximate chemical formula for this ester is $C_{52}H_{53}O_{13}$. In C_6 units this becomes $C_6H_{6.115}O_{1.5}$.

The soft resin of *X. hastilis* may consist chiefly of a polymer of *cinnamyl p-couma-rate*.^[4,6,15] The bulk of this resin may be a polymerization product of a variety of compounds isolated from this resin. See Table 2.

Trace compounds are present in *Xanthorrhoea* resins, many of which are strikingly similar to other compounds present in greater amounts (see Figure 4). *X. hastilis* contains *benzoic acid*,^[8] *X. resinosa* contains free cinnamic and *p*-coumaric acids,^[13] and *X. preissii* contains approximately 2 percent pinocembrin^[6,15] (C₁₅H₁₂O₄, $\Delta_{\rm f}$ H° –642.3 kJ/mole^B). The red coloration of the resins may be due, in part, to the presence of 4',5,7-trimethoxyflavan^[4]

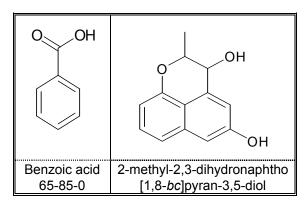


Figure 4. Minor compounds present in some Xanthorrhoea resins.

 $(C_{18}H_{20}O_4)$ and to *chrysophanic acid* $(C_{15}H_{10}O_4)$, which is present possibly as a result of bush fire damage,^[16] but has also been detected in *X. australis* resin that was undamaged by fire.^[6] *X. australis* also contains 2-methyl-2,3-dihydronaphtho[1,8-*bc*]pyran-3,5-diol, which is unstable in the presence of light and air yielding red resins.^[6] See Figure 4.

Ethanol insolubles range from 6.6%–7%,^[25,26] moisture 5.0%,^[25] and ash less than 2%.^[26] Unprocessed *X. hastilis* resin has up to 25 percent foreign matter such as husks and sand,^[6] and approximately 23 percent of unprocessed *X. resinosa* resin derived from its "bark" is foreign matter.^[13]

In the past, it was thought that supplies of this resin would last forever: "This resin is obtainable in inexhaustible quantities as the plants producing are abundant throughout Australia",^[5] and "By suitable conservation of the trees a continuous supply could be maintained."^[3] More recent perception is that acaroid resin is "a product of bush plants not suitable to cultivation; thus, a non-renewable resource with very limited availability."^[7]

Acaroid resin is currently used in pyrotechnics,^[3,9,27] and in the past was used in lacquers,^[3,5,22] sealing waxes,^[3,5,8,22] in the manufacture of picric acid,^[3,8] and in the manufacture of the dye *nitropicric acid*, where up to $\frac{1}{2}$ of the weight of the resin may yield dye.^[5] See Table 3.

Shellac

Shellac (9000-59-3), also called *lacca*, *lac*,^[28] *garnet lac*, *gum lac*, and *stick lac*,^[29] is a resinous secretion of the insect *Laccifer lacca*,^[28,29] which is continuously produced by the insect after consumption of the juices of the host tree *Kusum* (*Schleichera trijuga*).^[30] Its composition varies with the season.^[28] Shellac is a combination of a hard resin secreted at a regular rate and a soft resin secreted at an irregular rate.^[30]

Shellac contains 67.9% C, 9.1% H, and 23.0% O according to one reference,^[30] and 67.0% C, 9.00% H, 23.87% O, and 0.13% ash according

to another.^[31] This corresponds to formulas of $C_6H_{9.58}O_{1.53}$ and $C_6H_{9.60}O_{1.60}$, respectively. The primary constituent of shellac is *aleuritic acid* (533-87-9, $C_{15}H_{30}O_4$, $\Delta_f H^o$ –1237.1 kJ/mole^B), which accounts for up to 43% of the resin.^[30] It is uncertain if shellac truly contains *shellolic acid* (4448-95-7, $C_{15}H_{20}O_6$)—reported in the past,^[32] as some researchers have been unable to isolate it.^[30] See Figure 5. Other acids are present, but their exact percentages have not been worked out.^[30] In addition, waxes are present in amounts ranging from 3.5 to 5.5 percent, and are secreted in the form of long filaments.^[30] Again, the results of the analysis of

Table 4. Δ _f H ^o of Shellac ^[a] Derived from Pyrotechnic Colored Flame Formulations and Flame
Temperatures.

	Temp	$\Delta_{\rm f} {\sf H}^{\sf o}$	Temp (K)	Flame Temp.
Color Agent	(K ^[b])	(kJ/mole ^F)	(–440 kJ/mole)	Percent Error
SrCO ₃	2475	-401	2458	0.7
SrC ₂ O ₄ ·H ₂ O ^[c]	2440	-443	2441	0.0
SrCl ₂ ·6H ₂ O	2475	-238	2387	3.6
Sr(NO ₃) ₂	2625	-247	2573	2.0
Na ₂ CO ₃	2460	-485	2479	-0.8
NaHCO ₃	2480	-419	2472	0.3
Na ₂ C ₂ O ₄	2450	-518	2484	-1.4
NaCl	2540	-283	2476	2.5
BaCO ₃	2430	-581	2491	-2.5
BaC ₂ O ₄	2430	-569	2487	-2.5
BaCl ₂ ·2H ₂ O	2390	-588	2459	-2.9
Ba(NO ₃) ₂	2525	-603	2575	-2.0
CuCO ₃ ·Cu(OH) ₂	2430	-493	2452	-0.9
CuSO ₄ ·5H ₂ O	2390	-463	2401	-0.5
Cu (10%)	2460	-372	2430	1.2
Cu (5%)	2540	-343	2501	1.5

Shellac, C₆H_{9.6}O_{1.6}^[a], -440 kJ/mole^F, standard deviation = 119.8 kJ/mole^F.

- Notes: The copper-arsenic coloring agent formulations were not used due to the computer program^[33] not including the element arsenic. Copper oxalate, $CuC_2O_4 \cdot H_2O$, was not used due to an $\Delta_f H^\circ$ value being unavailable at the time of this writing. One atmosphere (1 Bar) was used in all runs.
- [a] $C_6H_{9.6}O_{1.6}$, from Shimizu.^[31]
- [b] Flame temperatures from the graphic chart "Figure 48 Flame Temperature with Various Coloring Agents",^[31] and is estimated to approximately ±10 K accuracy.
- [c] $\Delta_{\rm f}$ H° data was not found for strontium oxalate hydrated by a single water molecule. The value used, -1666.24 kJ/mole, was interpolated from values for no hydration,^[34]-1370.68 kJ/mole, and 2.5 water molecules,^[35]-2109.57 kJ/mole.

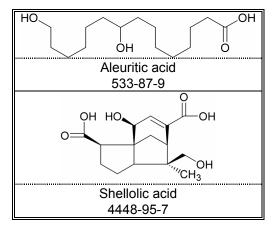


Figure 5. Constituents of shellac.

the waxes give conflicting results.^[30] Neither shellolic acid or the waxes will be considered here due to these circumstances.

Shimizu made a series of flame temperature measurements of various salts used in the production of colored flames.^[31] Shellac was used as the fuel/binder in many of them. Most of the formulations using ammonium perchlorate as an oxidizer were used as input for a free energy minimization program,^[33] and from these computer codes the $\Delta_{\rm f} {\rm H}^{\rm o}$ was "reverse-engineered". See reference 1 for details on this method and a summary of important assumptions regarding its use.

Table 4 presents the coloring agent, the measured flame temperatures,^[31] and the reverseengineered $\Delta_f H^\circ$ values. An average value of – 440 kJ/mole, standard deviation of 119.8 kJ/mole, was estimated using this method. An $\Delta_f H^\circ$ of –396 kJ/mole was calculated using equation 5 from reference 1, which is based on an analysis of 337 different CHO compounds. Clearly, either of these methods should only be used when laboratory-based values are unavailable and other estimation methods are not practical. Shellac is used in pyrotechnic compositions^[9,27,31]—probably less now than in the past due to its high cost,^[9] and in a variety of varnishes, sealants, and cements.^[28,29]

Charcoal

Charcoal is the solid, carbonaceous residue left remaining after the destructive distillation of carbonaceous materials.^[36] The source material may be of animal, vegetable, or mineral origin. The charcoal outlined here is derived from wood or wood products. This charcoal is not to be confused with the briquette form used in outdoor grills, which typically contains many additional compounds and up to 25 percent ash.^[37] A commercial brand of charcoal used in outdoor cooking contains wood charcoal, anthracite coal, mineral charcoal, starch, sodium nitrate, limestone, sawdust, and borax^[38]—almost a pyrotechnic formulation in itself!

Hardwood charcoal is manufactured batchwise in kilns or continuously in a furnace^[36,37,38] by a four-step pyrolysis process. Heat is applied to the wood, and as the temperature approaches 100 °C, water and volatile hydrocarbons are released and distilled. Once the moisture content of the wood has been removed, the temperature of the wood rises higher, and the hydrocarbon distillate yield increases. This second stage continues to approximately 275 °C. At this temperature the third stage begins, and external application of heat is no longer required as the carbonization reactions become exothermic. The bulk of the hydrocarbon distillates are produced as the temperature increases to 350 °C. The exothermic reactions then end, and once again heat is applied to bring the charcoal to its final processing temperature, which is typically between 400 and 500 °C. At these temperatures the less volatile tars and pitch are removed from the product.^[36]

Distillation	Charco	Yield		
Temp (°C)	С	Н	0	(%)
200	52.3	6.3	41.4	91.8
300	73.2	4.9	21.9	51.4
400	77.7	4.5	18.1	40.6
500	89.2	3.1	6.7	31.0
600	92.2	2.6	5.2	29.1
700	92.8	2.4	4.8	27.8
800	95.7	1.0	3.3	26.7
900	96.1	0.7	3.2	26.6
1000	96.6	0.5	2.9	26.3

Table 6. Typical Charcoal Composition and Yield as a function of Temperature	[36]
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If dry, ash-free wood is assigned the approximate formula $C_{42}H_{60}O_{28}$, then the following generalization of wood pyrolysis may be written:^[36]

$\begin{array}{c} 2 \ C_{42}H_{60}O_{28} \ \rightarrow \\ (wood) \end{array} \end{array} \rightarrow$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	
(carbon	+ 3 CO + $2 \text{ C}_2\text{H}_4\text{O}_2$ + (carbon (acetic acid) monoxide)	
CH₃OH (methar	+ C ₂₃ H ₂₂ O ₄ nol) (wood tar)	

These products are divided into four categories: charcoal, noncondensible gases, pyroligneous liquor, and insoluble tars. The distribution of these products varies depending on the raw materials used and the pyrolysis conditions. Table 5 lists a typical distribution. Pyrolysis temperature plays a key role in the composition of the charcoal. As expected, higher pyrolysis temperatures result in higher carbon percentages and lower charcoal yields—see Table 6.

Charcoal composition varies not only due to the source material and pyrolysis conditions, but even within individual pieces of wood: one report^[39] states that a 5 cm stick of elder charcoal had 45% volatiles at the edge, but only 30% at the midsection. In an analysis of different lots of maple charcoal from the same manufacturer, it was demonstrated that significant variations in composition, ash content, and heating values existed, where the latter varied 13%.^[40] Charcoal used in the manufacture of black powder has no exact specification, but the industries manufacturing it generally conform to a composition of 75% ±5% carbon and a volatile content

Table 5. Typical Yields of Various FinalProducts per 1000 kg of Dry Wood.

Product	Unit	
Charcoal	kg	300
Pitch	kg	33
Soluble tar	liter	91.8
Ethyl acetate	liter	61.3
Creosote oil	liter	12.5
Methanol	liter	12.5
Ethyl formate	liter	5.4
Methyl acetate	liter	4.2
Methyl acetone	liter	2.9
Ketones	liter	0.8
Allyl alcohol	liter	0.4
Noncondensible gas	meter ³	156

of 20–30%.^[39] See Tables 7 and 8 for representative elemental compositions, $\Delta_f H^o$ values, and computed oxide-form ash compositions.

Wood charcoal is used in fireworks,^[9,27,31] in the manufacture of black powder,^[9,29,39,40] in cast iron production,^[37] as a fuel for outdoor cooking,^[29,36–38] and as a filtering medium (activated carbon).^[29,36]

	Temp.		E	Iemental A	Analysis			HHV	$\Delta_{\rm f} {\rm H^o}$	
Source	°C	С	Н	0	Ν	S	Ash	MJ/kg	MJ/kg ^H	Ref.
Pine ^[a]	400	75.3	3.8	15.2	0.8	0.0	3.4	28.1	-1.95	41
Pine ^[a]	500	80.3	3.1	11.3	0.2	0.0	3.4	31.1	0.41	41
Redwood	485 ^[b]	75.6	3.3	18.4	0.2	0.2	2.3	28.8	-0.66	42
Redwood	700 ^[b]	78.8	3.5	13.2	0.2	0.2	4.1	30.5	-0.29	42
Oak	NA	67.7	2.4	14.4	0.4	0.2	14.9	24.8	-0.80	42
Oak	NA	70.59	2.92	13.25	0.61	0.04	13.05	25.6	-1.66	40
Maple ^[c]	NA	71.96	2.06	15.27	0.46	0.03	10.22	26.7	0.20	40
Maple ^[c]	NA	76.87	3.49	16.03	0.32	0.01	3.30	29.2	-0.93	40
Maple ^[c]	NA	79.44	3.39	14.18	0.32	0.02	2.65	29.9	-0.93	40
Pine	750	88.4	7.8	2.88 ^[d]	0.4	0.2	0.32	NA	NA	32
Willow	NA	82.2	3.5	10.35 ^[d]	0.3	0.05	3.6	NA	NA	32

Table 7. Composition, Heating Value, and $\Delta_f H^\circ$ of Charcoals.

[a] Georgia Tech. Research Institute's "Tech-air" process using pine bark and sawdust

[b] Range of 694–822 K, an average of 485 °C used, and 733–1214 K, average of 700 °C used

[c] Sample #5—lowest percentage of carbon, #10—median, and #7—highest percentage of carbon of lots

[d] Oxygen by difference

Pitch

Pitch is a tar-like material produced from the destructive distillation of coal or biomass such as wood or wood by-products. It may be best described as "an awesome mixture of phenolic and nonphenolic compounds that has taxed the capabilities of several analytical laboratories for over a century."^[43] The names tar and pitch seem to be used in the literature almost interchangeably. Very little data is available for biomass tars.^[44] Pitch is a resin-based deposit of a widely varying and complex composition, and its analysis is made difficult because of this.^[45] Sedimentation tar is fractionated into tar oils and tar pitch, and hundreds of compounds have been identified.^[43] Data for a few pyrolytic oils is available, and is summarized in Table 9. Pitch that is a by-product of the pulping industry is generally considered a

nuisance, clogging the machinery and reducing the quality of the paper produced.^[45]

Shimizu^[31] refers to two different types of pitch used in pyrotechnic formulations, Pine Root Pitch I and II. They are apparently derived from oil of turpentine.^[27] An elemental analysis is provided for Pine Root Pitch II, however, Pine Root Pitch I was used in pyrotechnic formulations for flame temperature measurements. If the assumption is made that the elemental analysis is approximately the same for both varieties, then an $\Delta_f H^{\circ}$ may be estimated from the ammonium perchlorate based pyrotechnic composition in a manner similar to that used for shellac (see Shellac above; see reference 1 for important assumptions in this method's use). The resulting formula is $C_6H_{6,54}O_{1,03}$, Δ_fH° –221 kJ/mole^F. This compares favorably to -196.9^{E} kJ/mole. Naturally, this should be considered a

Table 8. Charcoal Ash Composition, Computed Percentage Oxide Form.^[40]

Source	CaO	SiO ₂	Al ₂ O ₃	K₂O	Fe ₂ O ₃	MgO	Na ₂ O	P_2O_5	TiO ₂	Li ₂ O (ppm)
Maple ^[a]	40.44	25.73	13.53	10.45	3.33	2.85	1.74	1.63	0.30	1084
Oak	49.20	25.09	13.36	6.57	1.95	1.71	0.87	1.01	0.24	434

[a] Sample numbers 1, 3, 5, 7, and 9 were normalized to 100% ash recovered, then averaged.

	Ele	menta	I Comp	ositic	n	HHV	$\Delta_{\rm f} {\rm H^o}$	C ₆ -basis	$\Delta_{f}H^{o}$	
Source	С	Н	0	Ν	S	MJ/kg	MJ/kg ^H	Formula	kJ/mole	Ref.
Tech-air oil ^[a]	39.5	7.5	52.6	0.1	0	24.3	0.73	C ₆ H _{13.58} O ₆ N _{0.01}	133 ^H	46
Biomass oil	59	7	32	1	0.1	24.656	-4.59	$C_6H_{8.48}O_{2.44}N_{0.09}S_{0.004}$	–56 ^H	47
Tech-air oil	65.6	7.8	25.6	0.9	0.1	22.8	-9.73	$C_6H_{8.5}O_{1.76}N_{0.07}S_{0.003}$	–1070 ^H	41
#6 Heating oil ^[b]	85.7	10.5	2.0	—	1.8	42.3	-0.77	C ₆ H _{8.76} O _{0.11} S _{0.05}	-65 ^H	47
Pine root ^[c]	75.12	6.87	17.14		—	—	-2.3	C ₆ H _{6.54} O _{1.03}	–221 [⊧]	31

Table 9. Pyrolytic Oil Compositions, Heating Values, and $\Delta_{\rm f} {\rm H}^{\circ}$.

Note: All oils are liquid except Pine root.

[a] Oil produced at approximately 500° C.

[b] Included for comparison.

[c] Pitch. Included for comparison to pyrolytic oils. See text.

very tentative estimate due to the aforementioned assumption and the single data-point used.

Pitch is used in pyrotechnic compositions^[27,31]—perhaps more so in Japanese fireworks than in the west,^[27] and also in sealants, roofing compounds, and wood preservatives.^[29,43]

Gilsonite

Gilsonite (12002-43-6), also known as *uin-tahite*^[48,49] and *North American Asphaltum*,^[50] is a black, homogenous, solid hydrocarbon that is *asphaltene*-rich.^[48,50,51] It is mined in north-eastern Utah near the junction of the White and Green rivers south of Vernal, in an area approximately 3600 km^{2.[48]} It is found in vertical veins (dikes) that vary in width from millimeters up to 5.5 m, and up to 13 km in length. The Cowboy vein is the widest, measuring 5.5 m wide at its maximum, a depth of 305 m, and is

estimated at containing over 16 million metric tons (includes the neighboring Bonanza vein).^[49]

Gilsonite is sorted into the grades *Selects*, *Seconds*, and *Jet*.^[49] The selects are taken from the center of the vein, and the seconds are taken from near the vein walls. Jet is mined from the middle of the Cowboy vein, and is characterized by a deep black color with bluish undertones. The fusing-point temperature increases, whereas the petroleum naphtha solubility decreases, from selects to seconds to jet.^[49] Gilsonite, as mined, is almost completely free of mineral impurities.^[48] Impurities present include vanadium, nickel, iron, and copper. The vanadium and nickel contribute the most, and even then typically average less than 100 ppm each.^[51,52]

Gilsonite is part of a group of related bitumens including *ozocerite*, *asphalt*, *glance pitch*, and *grahamite*. They are all members of the maceral subgroup *asphaltite*, which is a *migrabitumen*.^[51] See Table 10 for compositions and $\Delta_{\rm f} {\rm H}^{\circ}$. Gilsonite is used in pyrotechnics,^[27] as a binder for wood fibers,^[48] as an oil substitute for paints and varnishes,^[48,49] in the production of electrode coke and high-octane gasolines,^[48,49] in asphalt paving products,^[29,48] and as a high-energy component of certain explosives.^[48]

Wax

Wax is a low melting-temperature mixture of organic compounds of high molecular weight that typically repels water and is soluble in hydrocarbons.^[29] Waxes may be of animal, vegetable, mineral, or synthetic origin.^[29]

Wax is a naturally occurring fraction of petroleum. There are two general types of petroleum waxes: *paraffin* (untreated 8002-74-2, clay-treated 64742-43-4) waxes in petroleum distillates and *microcrystalline* (clay-treated 64742-42-3) waxes in petroleum residues.^[51] Paraffin wax is a solid crystalline mixture of predominantly straight-chain hydrocarbons^[51] ranging from C₂₀ to C₃₆.^[54] Microcrystalline wax hydrocarbons range from C₃₀ to C₇₅.^[54] *Cyclic* and *dicyclic* hydrocarbons are also present.^[30,55] The composition of the wax varies with the particular wax-bearing crude oil from which it is derived.^[55]

The simplest description of a paraffin wax would be an *alkane* with an approximate formula of C_nH_{2n+2} . This would result in a range of $C_{20}H_{42}$, $\Delta_f H^o$ –622.86 kJ/mole^B to $C_{36}H_{74} \Delta_f H^o$ – 1093.42 kJ/mole^B. In C_6 units this becomes $C_6H_{12.6} \Delta_f H^o$ –186.9 kJ/mole^B to $C_6H_{12.3} \Delta_f H^o$ – 182.2 kJ/mole^B. For microcrystalline wax, the

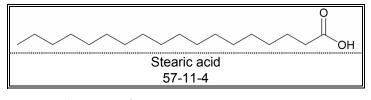


Figure 6. Stearic acid.

corresponding ranges would be $C_{30}H_{62}~\Delta_{f}H^{o}-916.96~kJ/mole^{B}$ to $C_{75}H_{152}~\Delta_{f}H^{o}$

-2240.41 kJ/mole^B, or in C₆ units C₆H_{12.4} Δ_f H° -183.4 kJ/mole^B to C₆H_{12.16} Δ_f H° -179.2 kJ/mole^B. If the *assumption* is made that paraffin wax is C₂₀H₄₂, then the Δ_c H° of -46.61 MJ/kg^[56] leads to a Δ_f H° of -682.5 kJ/mole^C, or in C₆ units, C₆H_{12.6} Δ_f H° -204.8 kJ/mole^C, which is in reasonable agreement with the Benson Group based estimates.

Paraffin wax from a solvent de-waxing operation is commonly called "*slack wax*" (64742-61-6)^[51] and may be categorized as *light neutral* and *heavy neutral*.^[54] Slack wax may have between 5 and 50% oil content, which is removed such that the fully refined petroleum wax has an oil content of 0.5% maximum.^[54] If paraffin oil is *assumed* to have an approximate composition of C₂₀H₄₂, then the Δ_c H° of -41.00 MJ/kg^[56] leads to an Δ_f H° of -2294 kJ/mole_{liquid}^C, or in C₆ units, C₆H_{12.6} and Δ_f H° -688.2 kJ/mole_{liquid}^C.

Petrolatum (8009-03-8), also known as petroleum jelly, white petroleum jelly, Vaseline, and Stanolene,^[28] is a colloidal system containing both non-straight chain solid hydrocarbons and high-boiling liquid hydrocarbons,^[28] and is a low-melting microcrystalline wax.^[51] The microcrystalline hydrocarbons of petrolatum wax range from C₃₃ to C₄₃^[29] with an approximate

Table 10. Elemental Composition, Heating Value, and $\Delta_f H^\circ$ of Bitumens.

	Elemental Composition			HHV	$\Delta_{\rm f} {\rm H}^{\rm o}$	C ₆ -basis	$\Delta_{\rm f}{\sf H}^{\sf o}$				
Bitumen	С	Н	0	Ν	S	Ash	MJ/kg	MJ/kg ^H	Formula	kJ/mole ^H	Ref
Gilsonite	84.9	10.0	1.4	3.3	0.3	0.1	41.64	-0.325	$C_6H_{8.42}O_{0.07}N_{0.2}S_{0.008}$	-27.6	50
bitumen ^[a]	84.44	11.05	2.59 ^[b]	1.00	0.75	0.17	41.87	-1.47	$C_6H_{9.36}O_{0.14}N_{0.06}S_{0.02}$	-125.2	53
bitumen	83.1	10.6	1.1	0.4	4.8	0.75	40.71	-1.93	$C_6H_{9.12}O_{0.06}N_{0.02}S_{0.13}$	-167.1	51

[a] P.R. Springs bitumen

[b] Oxygen by difference

formula of C_nH_{2n+2} .^[28] The liquid form is *white mineral oil* (8012-95-1).^[29] Aromatic compounds are highest in petrolatum (43%) and lowest in light neutral wax (3.2%).^[54] Composition data sufficient to render an $\Delta_f H^\circ$ estimate was not found as of the time of this writing. The $\Delta_f H^\circ$ probably lies somewhere between paraffin wax (solid) and paraffin oil (liquid). The average of the aforementioned values based on the *assumed* composition of C₂₀H₄₂, in C₆ units, would be C₆H_{12.6} $\Delta_f H^\circ$ –447 kJ/mole_{solid-liquid}^C.

Beeswax (white 8012-89-3, yellow 8006-40-4), is produced by various species of honeybees including *Apis mellifera*, *A. dorsata*, *A. flores*, and *A. Indica*. ^[30,57] Beeswax contains a variety of different compounds, each with a range of molecular sizes. See Figure 7 and Table 11. [Note that most of the renderings in Figure 7 use an abbreviated notation, (CH₂)_x, which indicates that this CH₂ unit repeats "x" times, where "x" is variable. Without this notation, the renderings would be lengthy and difficult to compare to each other.] The resulting formula based on this tabulated data is $C_{39,285}H_{78,296}O_{2,369}$ $\Delta_f H^{\circ}$ -1588.3 kJ/mole^B, or in C₆ units, C₆H_{11.958}O_{0.362}, $\Delta_f H^{\circ}$ -242.6 kJ/mole^B.

Paraffin waxes are used in pyrotechnics,^[27,31,55] polishes, candles, crayons, paper coatings, packaging, and waterproofing.^[29,54] Beeswax is used in cosmetics,^[29,30,57] candles, shoe polish and polishes,^[28–30,54] and furniture and floor waxes.^[29] Petrolatum and paraffin oil are occasionally used in fireworks as *phlegmatizers*.^[27] Other waxes are also used in pyrotechnics: *kauri* wax, *carnauba* wax,^[55] and *stearic acid* (57-11-4, *octadecanoic acid*, C₁₈H₃₆O₂, Δ_{f} H^o –947.7 kJ/mole,^[24] see Figure 6) to name a few.^[9,27]

Component	Weight Percent ^[a]	Typical Ranges	Representative Value ^[b]	∆ _f H⁰ kJ/mole ^B
hydrocarbons	14	C ₂₃ –C ₃₁	C ₂₉ H ₆₀	-887.55
monoesters	35	C ₃₈ -C ₅₂	C ₄₆ H ₉₂ O ₂	-1724.39
diesters	14	C ₅₆ –C ₆₆	C ₆₀ H ₁₁₉ O ₄	-2477.41
triesters	3	NA	C ₆₀ H ₁₁₈ O ₆	-2822.28
hydroxymonoesters	4	$C_{24} - C_{34}$	$C_{30}H_{61}O_3$	-1182.57
hydroxypolyesters	8	NA	$C_{46}H_{92}O_5$	-2274.33
acid monoesters	1	C ₁₆ –C ₂₀	C ₁₆ H ₃₀ O ₄	-1243.0
acid polyesters	2	NA	C ₃₀ H ₅₆ O ₆	-2005.02
free acids	12	C ₁₄ –C ₃₆	$C_{27}H_{52}O_2$	-1216.23
3-hydroxyflavanone	0.3	C ₁₅	$C_{15}H_{12}O_3$	-418.88
unidentified	6.7 ^[c]	NA	NA	NA

 Table 11. Beeswax Composition and Formation Enthalpies.

[a] All Weight Percentages and Typical Ranges from reference 57 except 3hydroxyflavanone from reference 30. The unidentified component was given the value of 7 percent in reference 57, however, the author assigned it a value of 6.7 percent to account for the 3-hydroxyflavanone.

- [b] Specific formula chosen by the author as representative of this component. See Figure 7 for the basic structures used in the estimates.
- [c] Excluded from the beeswax representative formula and its $\Delta_{f}H$.

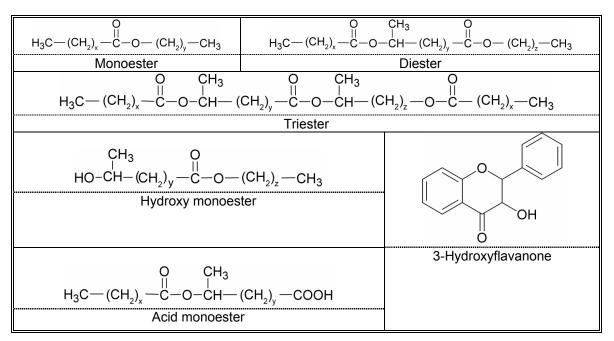


Figure 7. Some compounds contained in beeswax.

Miscellaneous Organic Compounds

Modern pyrotechnic compositions frequently utilize synthetic pure compounds and polymers. The choices made available by the chemical industries are truly remarkable. The polymers are made from a variety of different monomers in precisely controlled proportions. Blends of different polymers, and the introduction of additives such as plasticizers, stabilizers, ultraviolet light inhibitors, etc., make for a bewildering variety for the consumer to choose from. This is further complicated by the plethora of trade names given to each of these materials. For example, one reference^[58] lists no less than 359 different names for polyvinyl chloride!

A sampling of some common, pure compounds and polymers are considered here for these reasons. See Table 12 for formulas and $\Delta_f H^\circ$, and Figures 8–12 for representative structures.

Naphthalene (91-20-3) finds occasional use in pyrotechnics for the generation of smoke,^[9,27] and is also used in the production of smokeless powder, moth repellants, and preservatives.^[29] *Anthracene* (120-12-7) is also used for smoke generation,^[27] and is a carcinogen.^[29]

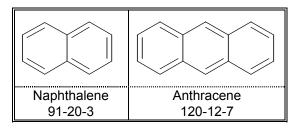


Figure 8. Naphthalene and anthracene.

Hexamethylenetetramine (100-97-0), also known as *hexamine* and *methenamine*,^[9,29] is used in some pyrotechnic star formulations,^[9] in the manufacture of adhesives, and in the high explosive *cyclonite*.^[29]

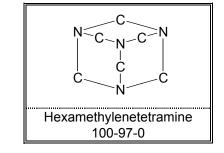


Figure 9. Hexamethylenetetramine.

Gallic acid (149-91-7) is used in the generation of pyrotechnic whistle effects,^[27] in photography, and in the manufacture of tannins, inks,

		$\Delta_{\rm f} {\sf H}^{\sf o}$	C ₆ Basis	$\Delta_{\rm f} {\rm H^o}$	
Compound	Formula	kJ/mole	Formula	kJ/mole	Ref.
Naphthalene	C ₁₀ H ₈	77.9	C ₆ H _{4.8}	46.7	24
Anthracene	C ₁₄ H ₁₀	129.2	C ₆ H _{4.286}	55.4	24
Hexamethylenetetramine	$C_6H_{12}N_4$	124.1	$C_6H_{12}N_4$	124.1	24
Poly(vinyl chloride)	C ₂ H ₃ Cl	-96.90 _{liguid} B [a]	C ₆ H ₉ Cl ₃	–290.7 ^{B [a]}	
Poly(vinylidene chloride)	$C_4H_5CI_3$	-224.43 _{liguid} ^{B [a]}	C ₆ H _{7.5} Cl _{4.5}	–336.6 ^{B [a]}	
Hexachlorobenzene	C ₆ Cl ₆	-127.6	C ₆ Cl ₆	-127.6	24
Gallic acid	C ₇ H ₆ O ₅	-959.0	C ₆ H _{5.143} O _{4.286}	-822.0	23
Sodium benzoate	C ₇ H₅NaO ₂	-595.38	C ₆ H _{4.286} Na _{0.857} O _{1.714}	-510.3	60
Sodium salicylate	C ₇ H₅NaO ₃	–795.2 ^{PB}	C ₆ H _{4.286} Na _{0.857} O _{2.571}	–681.6 ^{PB}	
Tristearin	$C_{57}H_{110}O_6$	–2276.1 ⁸	$C_6H_{11.579}O_{0.632}$	–239.6 ^B	

Table 12. Composition and $\Delta_f H^\circ$ of Miscellaneous Organic Compounds.

[a] Required Benson Group values were unavailable for the solid phase.

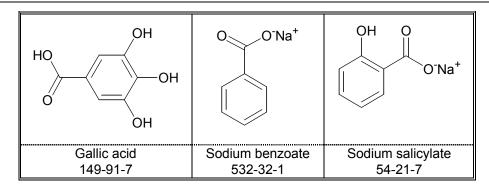


Figure 10. Gallic acid, sodium benzoate and sodium salicylate.

and dyes.^[29] Sodium benzoate $(532-32-1)^{[9]}$ and sodium salicylate $(54-21-7)^{[9,27]}$ are also used in pyrotechnic whistles. The former is used as a food preservative and the latter as a preservative for adhesives.^{29]}

Polyvinyl chloride (9002-86-2), or *PVC*, is used in pyrotechnics as a *chlorine donor*^[9,27] and as a fuel,^[29] as a *plastisol* binder in composite propellants,^[59] and in the manufacture of piping, siding, and plastic products.^[29] *Polyvinyli*- *dene chloride* (9011-06-7), also known as *Saran*,^[9,29] is also used as a chlorine donor in pyrotechnics,^[9,27] for food packaging films, and in upholstery and fabrics.^[29] *Hexachlorobenzene* (118-74-1) once found use in pyrotechnics as a chlorine donor,^[9,27] but its use has declined due to a preference for PVC.^[27] It is likely a carcinogen. ^[9] It is also used for fungicides and wood preservatives.^[29]

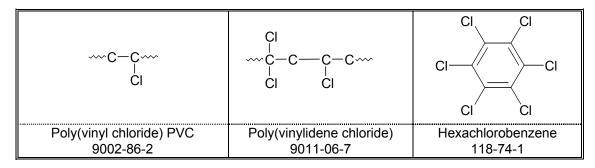
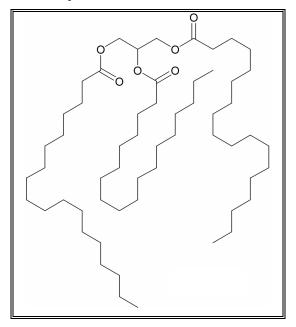
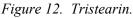


Figure 11. Polyvinyl chloride, polyvinylidene chloride and hexachlorobenzene.

Tristearin (555-43-1), also known as *stearin* and *glycerol tristearate*,^[9,29] is used in pyrotechnics as a phlegmatizing agent and for coating aluminum flakes,^[9] and in soap, candles, adhesives, and polishes.^[29]





Conclusion

A variety of disparate sources of data, as illustrated above, may be drawn on to gather, reduce, and estimate useful chemical formulas and formation enthalpies for fuels used in pyrotechnics until such time as exact, laboratory measured values become available. In this process of research and discovery, other potentially useful information may be found. For example, the trace elements present in many of the fuels might cause undesirable coloration of, say, a star's color purity. This ancillary information assists the energetics chemist in making informed decisions. It is the author's hope that the reader has a greater appreciation for the overall simplicity and variety of methods in which useful estimates may be made. The benefit one gets by estimating and using these values certainly outweighs the costs in getting them.

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(05/98)

Errata

Issue 8, Winter 1998, page 12, Table at bottom of page:

In the row for "Rhap" the "Formula" " $C_6H_{10}O_5$ " should be " $C_6H_{12}O_5$ ".

Page 15, Table 5 at top of page:

In the row for "Nitrate, DS = 2.5" the "Formula" "C₆H_{7.5}N_{2.5}O₂₀" should be "C₆H_{7.5}N_{2.5}O₁₀".

Page 16, Reference 23 that appears at the end, should be Reference 25 and subsequent references renumbered.

Events Calendar

Pyrote	chnics		
17 th Symp. on Explosives & Pyrotechnics	Grunelagen Pyrotechnik (Fundamentals of Pyrotechnics)		
April 27–29, 1999, Essington, PA, USA	May 17–22, 1999, Weil-am-Rhein, Germany		
Contact: Franklin Applied Physics, Inc. Phone: +610-666-6645 FAX: +610-666-0173 2 nd Workshop in the Use of Microcalo- rimetry to Characterize Energetic Materials	Contact:Dr. G. A. SchröderCarl-cranz-Gesellschaft e. V.79576 Weil-am Rhein, GermanyPhone:+49-7621-75091FAX:+49-7621-793026Web site:www.ccg.dlr.de		
May 17–19, 1999, Leeds, UK			
Contact:Dr. Trevor T. GriffithsPhone:+44-1959-51-5321FAX:+44-1959-51-6065e-mail:ttgriffiths@deragov.uk			

7th International Seminar—Groupe de Travail de Pyrotechnie—EuroPyro 99 and 25th International Pyrotechnics Seminar

June 7–11, 1999, Ensieta Brest, France

<u>Contact</u>: Association Francaise de Pyrotechnie EuroPyro 99 B.P. No. 121 45240 La Ferte St. Aubin, France

FAX: +33-238-516-822 Web site: www.intlpyro.org

30th Int'l Annual Conference of ICT

June 29–July 2 1999

<u>Contact</u>: Mrs. Gesa Langer, Chair Franuhofer-Inst. für Chemische Technologie Attn: Manuella Wolff PO Box 1240 D-76318 Pinfztal (Berghausen) Federal Republic of Germany

Phone:	+49-(0)721-4640-121
FAX:	+49-(0)721-4640-111
e-mail:	mw@ict.fhg.de
Web site:	www.ict.fhg.de

3rd International Conference On Intrachamber Processes And Combustion In Devices Using Solid Propellants and in the Gun Tube Systems (ICOC99)

July 7-9, 1999, Izhevsk, Udmurt Rep., Russia

Chemistry of Pyrotechnics & Explosives

July 25-30, 1999, Chestertown, MD, USA

Advanced Pyrotechnic Seminar: Pyrotechnics in the 21st Century — A Review of the State-of-the Art in 1999

Aug. 1–6, 1999, Chestertown, MD, USA

<u>Contact</u>: John Conkling PO Box 213 Chestertown, MD 21620, USA

Phone:	410-778-6825
FAX:	410-778-5013
e-mail:	John.Conkling@washcoll.edu

American Pyrotechnics Association Conv.

Oct. 19–23, 1999, Las Vegas, NV, USA

Contact: American Pyrotechnics Association PO Box 30438 Bethesda, MD 20824, USA Phone: 301-907-8181 FAX: 301-907-9148 e-mail: julie@fireworksafty.com Web site: www.americanpyro.com 26th International Pyrotechnics Seminar

Oct. 1-4, 1999, Nanjing, China

Contact: Jinhua Peng/Chongkai Sun, Chair.

Nanjing Univ. of Science and Technology

 Nanging, 210084 P. R. China

 Phone:
 86-25-431-5225

 FAX:
 86-25-443-1622

 e-mail:
 diecnust@publicl.ptt.js.cn

3rd International Autumn Seminar on Propellants, Explosives and Pyrotechnics

Oct. 5–8, 1999, Chengdu, China <u>Contact</u>: Prof. Feng Changgen, Mech. & Engr. Beijing Institute of Technology PO Box 327 Beijing, 100081, China FAX: +86-10-6841-2889 e-mail: cgfen@public.east.cn.net

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