

Miscellaneous Pyrophoric Substances

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This chapter will deal with a few additional spontaneously igniting substances. They act in this manner in what might be called their natural state or, more often, in a special condition of dispersion or preparation.

The alkali metals form a series having increasing tendency to spontaneous flaming with increase in atomic weight: Lithium and sodium will not ignite in air at ambient temperatures and even up to their melting points; potassium may oxidize so rapidly that it melts and ignites, especially when pressure is applied. The latter was the case when a 2-cm³ piece exploded and caught fire after several cuts had been made with a stainless knife. Rubidium will sometimes ignite in dry oxygen, and cesium burns in air as it is removed from an inert covering oil. The reactivity of the alkali metals is further increased when they are melted under an inert liquid hydrocarbon, such as xylene, of boiling point higher than the melting point of the metal, and the mixture is stirred vigorously. This process converts the bulk material into small globules.

That moisture in the air or in the oxygen plays some part in these oxidations is evident according to Holt and Sims from the fact that sodium or potassium can be distilled under oxygen that has been dried

with phosphorus pentoxide. Moreover, the burning metals are said to have their flame extinguished when "immersed" in thoroughly dried oxygen.

A more practical way of extinguishing alkali metal fires is to deprive them of oxygen by covering them with dry alkali chloride, soda ash, or graphite (carbon dioxide» carbon tetrachloride, and even sodium bicarbonate are useless or dangerous). Graphite takes a special place with molten potassium, since it is immediately wetted, swells up, and disintegrates the metal. If those mixtures are deprived of excess potassium by heating in vacuum, pyrophoric compounds are found to exist of unusual structure but of definable formulas, C_8K and $C_{16}K_{91}$. Similar "insertion" compounds of rubidium and cesium, from metal vapor over graphite, have been described more recently in a French article.

Hauffe discusses the surface oxidation of alkali metal, quoting the theory of Pilling and Bedworth that the smaller volume of the formed oxide is responsible for the progressivity of the reaction. On the other hand, where the oxide volume is greater as on some heavy metals, it forms a protective layer.

However, this theory does not explain the existence of pyrophoric iron or the phenomenon of pyrophoricity at all, as shown in Table 2 by a comparison of the ratio of volume of oxide to volume of element. Also, in analyzing the problem of autoxidation of the alkali metals, one must consider that quite different types of oxides result from burning of these metals in air, e.g. Li_2O , Na_2O_2 , KO_2 , RbO_2 , and CsO_2 .

Table 2

Ratio of Volume of Oxide to Volume of Element

(according to Pilling & Bedworth)

Na	0.32	Mg	0.84	Cu	1.70
K	0.51	Al	1.28	Si	2.04
Li	0.60	Pb	1.31	Fe	2.06
Sr	0.69	Th	1.36	Mn	2.07
Ba	0.78	Zr	1.55	Co	2.10
Ca	0.78	Ni	1.68	Cr	3.92

Sodium and potassium form alloys, among them a eutectic of — 12.3°C (9.95°F) freezing point with 77.2% potassium. This liquid alloy, perhaps because of its quickly renewable surface area, is spontaneously ignitable, especially if dropped from a few feet onto a wooden surface.

"NaK." (pronounced nack), as the eutectic is called, as well as the alkali metals in general, have found new interest as heat dissipating and heat transfer agents in nuclear reactors and in motor valve stems of internal combustion engines. These uses have led to a special series of articles in the literature on the subject of handling these substances and their properties.

The reactivity in air of the alkali metals is more or less preserved in their previously-described hydrides and also in a few little known compounds such as their silicides (W. Klemm 1948). Brauer describes the preparation of these compounds and characterizes them as follows: NaSi, self-flammable as loose powder; KSi puffs and flames in air; with water, all four (i.e. the silicides of Na, K, Rb, Cs) ignite explosively.

We turn now to the elements and compounds that in bulk, or in a more or less coarsely powdered state, are stable or at least are not spontaneously

ignitable. In order to convert them into the pyrophoric form, a variety of procedures are employed, all tending to increase the surface area of the substance.

When the azides of strontium or barium are heated in vacuum to 140° and 160°C respectively, nitrogen is released and the alkaline earth metals are formed. These very finely powdered particles of both strontium and barium will burst into flame on admission of air.

This formation of spontaneously ignitable strontium and barium has been reported by Tiede. He also mentions the decomposition of calcium and lithium azide under the same conditions, but remarks only that lithium azide is rather explosive on heating.

The following are a number of more generally applicable methods by which self-ignitable heavy metals and related substances can be produced:

1. Pyrogenic decomposition at "low" temperatures of organic salts such as tartrates. This process yields self-ignitable metal powders of small particle sizes.
2. Reduction at relatively low temperatures of finely powdered oxides by hydrogen,
3. Transformation of an alloy into a "sponge", or simply the alloying process itself, even if the other metal is inactive as in the case of some amalgams.
4. Electrolysis of solutions of certain metal salts, using a mercury cathode. The resulting amalgams or mixtures will yield pyrophoric metals after removal of the mercury by distillation.

Processes 1, 2, and 4 produce metal powders of very small particle

size, but the reason for the pyrophoric behavior is not yet fully understood in every instance. Some experiments seem to indicate that adsorbed hydrogen is the cause. In other cases, it is obvious that the metal of greatest purity is most ignitable and that the presence of hydrogen reduces activity. These differences are, however, not irreconcilable since they may be caused by the different ways in which the hydrogen atoms are bonded to the reacting metals.

Both Gmelin and Mellor quote a variety of conditions under which metals are produced as pyrophoric substances. An important observation in cited references is that mixtures of iron oxide with aluminum oxide will tolerate much higher temperatures (red heat) and still yield pyrophoric iron on reduction by hydrogen.

Increase of surface area by mere mechanical comminution may sometimes lead to self-flammable products. Such is the case in the ball-milling of certain stainless steels and of "misch metal" (cerium alloy) under a hydrocarbon. The process leads to formation of minute flakes with the character of bronzing powders. Spontaneous ignition after removal of the liquid in the case of the stainless steels is due to the absence of a passivating protective layer upon the newly created surfaces.

The best known pyrophoric metals (using the term in the sense of spontaneous ignitibility only) are lead, iron, nickel, and cobalt.

Self-flammable lead powder can be made by heating certain organic salts alone if care is taken to exclude air. Michael Faraday (1791 — 1867), in a delightful little volume of lectures," describes the "lead pyrophorus made by heating dry tartrate of lead in a glass tube closed at one end and

drawn to a fine point at the other and then sealed. On breaking the point and shaking out the powder, he demonstrated to his "juvenile auditory" how the finely divided lead burned with a red flash.

Beside the tartrate, other organic salts—notably the oxalate and the formate—yield the more easily produced pyrophoric metals, i.e. lead, nickel, and cobalt, if the pyrogenic decomposition is performed at "low" temperature. These organic salts or the oxides of nickel, cobalt, and iron, under hydrogen at about 300°C, also furnish the self-flammable metals, but in the case of iron, a pyrophoric ferrous oxide (FeO) may first appear by reduction with hydrogen as well as by reduction under carbon monoxide.

The reactivity of nickel is increased by converting it into a "sponge", also called "Raney" nickel, which is used as a catalyst in the hydrogenation of organic compounds. It is made by alloying nickel with aluminum in equal parts and removing the aluminum by dissolving it with an alkali. The residual spongy nickel must be kept under water or oil since it bursts into flame when dry. As a consequence of its manufacture from the alloy with aluminum, this pyrophoric metal always contains some aluminum and hydrogen. On removal of the latter by prolonged aeration of the water slurry, the material loses its pyrophoricity.

When nickel is deposited electrolytically on a mercury cathode, it appears to form an intermetallic compound containing about 24% nickel, but when the mercury is distilled off, finely divided, strongly pyrophoric nickel is formed. Iron and cobalt are deposited by electrolytic process from their salt solutions as very fine suspensions on mercury cathodes. The iron and cobalt so deposited possess pyrophoric properties.

Chromium, molybdenum, and uranium have also been described as pyrophoric, and Remy mentions that chromium, obtained in a finely divided state from the amalgam by distilling off the mercury, is pyrophoric in air. A recent (1964) Russian article refers to pyrophoric manganese and manganese nitride, made from manganese amalgam. The metal is obtained after removal of the mercury through vacuum distillation, the nitride when the removal is accomplished under nitrogen.

Evidence for the high reactivity of uranium and some uranium compounds is found in the report by Hartman, Nagy and Jacobson that uranium metal in thin layers ignites at room temperature within a few minutes after exposure, as do uranium hydride (UH_3) and thorium hydride (ThH_2).

Katz and Rabinowitch call the powdered uranium "usually pyrophoric", UO_2 (from uranium and water) "pyrophoric", and UH_3 "often pyrophoric and ignitable on moistening".

Recently, processes have been invented to produce metal powders in "ultrafine" condition, i.e. below 0.1μ particle size. The fuel-type metals such as aluminum, of an average size of 0.03μ are pyrophoric and must be kept under a hydrocarbon.

Cerium, thorium, and zirconium can be made truly pyrophoric by alloying. Cerium amalgams, the alloys of cerium and mercury, become solids if the cerium content exceeds 2%. At 8—10% cerium content, these amalgams are spontaneously flammable in air. Thorium and zirconium, when alloyed with silver, copper, or gold, become much more ignitable, bursting into flame on rubbing. Thorium-silver alloys in approximately a 1:1 proportion are actually self-igniting. These alloys of 40—60% thorium with silver, made by a sintering process of powders, are described by Raub and Engels. They also describe the alloys of thorium with copper or with gold as "less pyrophoric." Alloys of zirconium with silver, copper, or gold require a rubbing action in order to exhibit self-ignition, and the alloys of titanium with silver,

copper, or gold are stable.

Brief mention will be given to some self-flammable lower oxides of active metals. This curious fact—that even lower oxides of elements can exhibit a strong enough tendency to further oxidation so as to become spontaneously flammable—has been mentioned by Ephraim for indium oxide (InO) made by hydrogen reduction; chromous oxide (CrO) made by oxidation of the amalgam of the metal; and vanadium sesquioxide (V_2O_3). Ferrous oxide (FeO) has been mentioned above.

Fricke and Rihl have described pyrophoric, pure white ferrous hydroxide, $\text{Fe}(\text{OH})_2$, forming Fe_2O_3 when it had free access to air, but Fe_3O_4 on slow oxidation. The ferrous hydroxide is not stable even in absence of oxygen.

A pyrophoric iron sulfide made from hydrated iron oxide and hydrogen sulfide under gasoline has been described recently.

The easy flammability of some carbonized organic matter (tinder) is well known and can be increased when organic substances are heated with various additives in the absence of air. Such pyrophoric or semi-pyrophoric carbon had some practical uses in the past. Portable, self-flammable carbon-containing mixtures in sealed glass tubes are mentioned in the literature as late as the second half of the last century under the name of "the pyrophorus," a word that today is as good as forgotten.

Crass, in his description of the precursors of the modern match, goes into some detail on these mixtures. They included "Homburg's pyrophorus," a roasted mixture of alum, flour, and sugar, hermetically sealed, which was essentially an activated charcoal; and "Hare's pyrophorus," similarly made from Prussian blue heated to redness and immediately sealed. In 1865 Roesling patented a similar substance that, "packed in air-tight vessels," was to be sprinkled on the bowl of a pipe and brought to red heat by suction, thus lighting the pipe.

Up to this point, all pyrophoric behavior has been reported as taking place under ambient conditions, meaning the normal atmospheric pressure. When circumstances

are such that a metal is exposed to an active gas such as oxygen under greatly increased pressure, some metals may ignite at room temperature even in massive state. This has been reported for "cleaned" zirconium at oxygen pressures of 300 lb/in.² or higher and for Zircaloy-2 under certain conditions.