

# PYROTECHNIC SNAKES

TENNEY L. DAVIS

Massachusetts Institute of Technology, Cambridge, Massachusetts

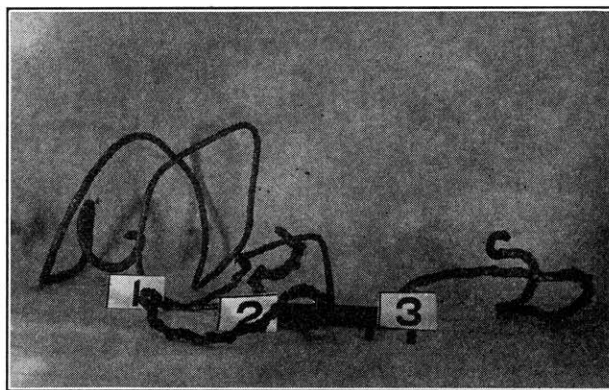
THE sale of the mercuric thiocyanate Pharaoh's Serpents,<sup>1</sup> with which many of us amused ourselves as children, is now forbidden by law in several of the states, for the vapors from these toys are poisonous, and, more serious, children have been known to eat them with fatal consequences. Many of the youngsters nowadays will have to wait until their high-school or freshman chemistry course before they can see a demonstration of the extraordinary property of the mercury salt. They can, however, purchase non-mercury Black Snakes, made entirely from organic materials, the composition of which is as much of a mystery to the generality of chemists as it is to the children who play with them.

Wöhler,<sup>2</sup> while still a medical student at Heidelberg in 1821, first reported the remarkable property of mercurous thiocyanate—which he prepared by precipitating mercurous nitrate with potassium thiocyanate—that it swells up when it is heated “winding out from itself at the same time worm-like processes, to many times its former bulk, of a very light material of the color of graphite, with the evolution of carbon disulfide, nitrogen, and mercury. On further heating the same material remains along with mercuric sulfide. The swollen mass obtained by gentle heating, when ignited with copper oxide, gives a gas consisting of carbon dioxide and nitrogen in the proportion in which they would be formed by the combustion of cyanogen”—and hence consists of paracyanogen.

Mercuric thiocyanate gives better snakes than the mercurous compound. When a heap or pellet of either of these substances is set on fire, it burns with an inconspicuous blue flame, producing sulfur dioxide and mercury vapor. The resulting pale brown or pale gray snake, if broken, is found to be much darker in the interior, and evidently consists of paracyanogen and mercuric sulfide, the mercury having been burned and vaporized from the outer layer.

Mercuric thiocyanate was first prepared by Berzelius<sup>3</sup> in 1821 by the action of thiocyanic acid on mercuric oxide. Claus<sup>4</sup> reported that mercurous thiocyanate is precipitated only in dilute solutions, that concentrated solutions of potassium thiocyanate and mercurous nitrate give a black precipitate which consists of metallic mercury mixed with mercuric thiocyanate. Otto

Hermes<sup>5</sup> appears to have been the first to report the preparation of pure mercuric thiocyanate by precipitation, although he suggests in his paper of 1866 that it was already in use in commercial *Pharaoschlängen* which, he says were made up with two per cent. of potassium chlorate. He stated that mercuric thiocyanate explodes powerfully when rubbed with an equal weight of potassium chlorate. The pure substance decomposes at 165°, but when mixed with one per cent. of potassium chlorate it decomposes at 90°. Philipp<sup>6</sup> in the following year reported further observations on mercuric thiocyanate: that it turns yellow when heated to 110°, that it is decomposed by light to form a gray material insoluble in hydrochloric acid and a dark colored material insoluble in potassium thiocyanate solution, that it is slightly soluble in hot water and comes out again on cooling in the form of thin pearly leaflets or small prisms which have all of the



BLACK SNAKES. NO. 1 FROM NAPHTHOL PITCH. NO. 2 FROM  $\beta$ -NAPHTHOL BY THE USE OF FUMING NITRIC ACID (1.50). NO. 3 FROM  $\beta$ -NAPHTHOL BY THE USE OF C.P. NITRIC ACID (1.42). NEAR THE NUMERAL 3 ARE TWO PELLETS LIKE THOSE FROM WHICH THE SNAKES WERE PRODUCED

properties of the precipitated material, and that it is soluble in cold hydrochloric acid and in potassium thiocyanate, potassium chloride, ammonium chloride, and mercuric nitrate solutions.

Since mercuric thiocyanate is soluble in an excess of the reagents from which it is prepared, it is best prepared by adding a potassium or sodium thiocyanate solution slowly and with stirring to a solution of mercuric nitrate to which a small amount of ferric chloride solution has been added. The appearance of the red

<sup>5</sup> HERMES, *J. prak. Chem.*, **97**, 477 (1866). The statement of Hermes, without experimental support, that the voluminous, snake-like residue consists of melam is evidently in error.

<sup>6</sup> PHILIPP, *Poggendorff's Ann. d. Phys. u. Chem.*, [5]**11**, 86 (1867).

<sup>1</sup> Compare “An historical account of Pharaoh's serpents,” by H. Irving in *Sci. Progress*, **30**, 62-6 (1935). I am indebted to Professor Ernest H. Huntress for calling my attention to this article.

<sup>2</sup> WÖHLER, *Gilbert's Ann. d. Phys. u. phys. Chem.*, **9**, 272 (1821). This is the same as Volume **96** of *Gilbert's Ann. d. Phys.*

<sup>3</sup> BERZELIUS, *Schweigger's J. f. Chem. u. Phys.*, **31**, 42 (1821). This is the same as Volume **1** of *Jahrbuch d. Chem. u. Phys.*

<sup>4</sup> CLAUS, *J. prak. Chem.*, **15**, 401 (1838).

color of ferric thiocyanate, if it is not dispelled by stirring, indicates that enough of the thiocyanate solution has been added. The white precipitate is collected, washed, dried, and powdered. The powder is moistened sparingly with a weak aqueous solution of gum arabic, "to which may be added a pinch of saltpeter,"<sup>7</sup> and is made into small cylindrical or conical pellets which are known as Pharaoh's Serpents' Eggs. If too much of the gum arabic water is used, the material assumes the consistency of heavy clay and is difficult to handle. On a plant scale, little truncated cones of the material are made by pressing the composition into holes, larger at one end than at the other, bored through a sheet of metal or a slab of hard wood, and then pressing the pellets out by means of a second board or sheet of metal studded with pegs which match the smaller end of the holes in the first piece. In the laboratory, pellets are made conveniently by means of two pieces of glass tubing, fire-polished at the ends; the wider piece about ten cm. long is supplied with a plug made from a cork stopper, which plug is to be moistened in order to move more freely when the instrument is in use, while the second tube about twelve cm. long fits within the other and is used as a plunger for pushing the cork plug. The composition is pushed into the tube against the cork plug; then, while the end of the tube is held against a flat surface, it is compressed to a compact pellet which is finally ejected by pushing the plunger.

"Snakes in the Grass," "Volcano Snakes," and so forth, depend upon the use of ammonium dichromate. If this material in the form of powder is made into a conical heap, and a flame applied to the top of it, a visible but not violent "combustion" proceeds through the mass which "boils up" to form a large volume of green material ( $\text{Cr}_2\text{O}_3$ ) resembling tea leaves. In practice, more flame is desired than ammonium dichromate alone will give. Weingart<sup>8</sup> recommends a mixture of two parts of ammonium dichromate with one of potassium nitrate and one of dextrine. Tin foil cones are made from circles of tin foil shaped on a former, and are introduced by means of the former into conical cavities in a block of wood; they are then about half filled with the powdered mixture, a Pharaoh's Serpent's Egg is pressed in, and the edges of the tin foil are turned down upon it to form the base of the cone. A shallow wooden box filled with the ammonium dichromate mixture in which five or six Serpent's Eggs are buried makes an amusing toy, and may be fired by means of a piece of blackmatch.<sup>9</sup>

Black non-mercury snakes were apparently first made commercially in Germany, and are at present fairly common in this country around the Fourth of July, in

<sup>7</sup> WEINGART, "Dictionary and manual of fireworks," Bruce Humphries, Inc., Boston, 1937, p. 152. This book contains many good formulas, and is recommended strongly to the chemist who wishes to try his hand at the making of fireworks.

<sup>8</sup> WEINGART, *loc. cit.*, p. 154.

<sup>9</sup> The black "fuse" made by passing a few pieces of cotton string, twisted together, through a slurry of finely pulverized black gunpowder and allowing to dry while stretched on a frame.

the form of "Barrel Snakes," "Hat Snakes" (black pellets affixed to black discs of pasteboard to form what look like miniature broad-brimmed black hats) "Colored Fire Snakes," and so forth. The first indication of the possibility of such snakes appears to be a report by Vorbringer<sup>10</sup> in 1867 that he had procured a brownish black product, which burned to form black snakes, by the nitration of a certain black, resinous, acidic material from coal tar, but he did not describe his raw material in such manner as to identify it and to make it available to others. The method of making black snakes was kept secret, and does not appear to have been described in accessible print until Weingart<sup>11</sup> published an account of it in 1937. Ten parts of powdered "naphtha pitch" is mixed intimately with two parts of linseed oil, seven parts of the strongest fuming nitric acid is added a little at a time, and the mixture is allowed to cool for an hour. The product is washed thoroughly with water, dried, powdered, mixed with three and one-half parts of powdered picric acid, and made into pellets with gum-arabic water.

Several questions at once suggest themselves. What is "naphtha pitch?" Will some more common material serve as well? What is the technic of nitrating twelve parts of material, largely solid, with seven parts of nitric acid? Is the linseed oil necessary, and what purpose does it serve?

Correspondence with various American manufacturers failed to discover anything which is known as "naphtha pitch." A sample of "naphthol pitch," a by-product of the manufacture of  $\beta$ -naphthol, was kindly supplied by the Calco Chemical Division of the American Cyanamid Company. This was a dark-brown, shiny, brittle material, having a conchoidal fracture and easily reduced to a cocoa-colored powder. In response to an inquiry as to how he carried out the nitration, Mr. Weingart replied that he "rubbed up the pitch with linseed oil in a Wedgewood mortar and added the acid, a little at a time, so as to avoid excessive heating"—and kindly sent a sample of the "naphtha pech" of German origin which he used in his own work.<sup>12</sup> This material was a dark brown, almost black, granular powder. Both the "naphthol pitch" and the "naphtha pech" reacted vigorously with nitric acid. When mixed with linseed oil and *nitrated by kneading* (if we may give a name to the technic), each yielded a friable product which burned to form a snake while a Bunsen flame was played upon it, but which did not maintain its own combustion. Powdered with picric acid and made into pellets as described, the

<sup>10</sup> VORBRINGER, *J. prakt. Chem.*, **102**, 187-8 (1867). This is an editorial note, signed "W" (Gustav Werther) based upon a letter from Vorbringer, describing experiments carried out in the laboratory of the *Mineralöl- und Paraffin-Fabrik des Herrn Dr. Hubner in Rehmsdorf bei Zeitz*.

<sup>11</sup> Weingart, *loc. cit.*, pp. 152-3.

<sup>12</sup> Mr. Weingart also stated that he had obtained satisfactory results by using, instead of "naphtha pech," the material procured by melting together sixty parts of Syrian asphalt and forty of roofing pitch. Worked up in the regular way, this "yielded fairly good snakes which were improved by rubbing the finished product up with a little stearine before forming into pellets."

product from each yielded excellent snakes, smooth-skinned and glossy with a luster like that of coke, elastic, and of spongy texture within. The pellets burned with a luminous, sooty flame; a pellet one cm. long and eight mm. in diameter gave a snake about 1.3 meters in length.

A satisfactory procedure was found to be as follows. Ten grams of powdered naphthol pitch is mixed intimately with two grams of linseed oil, and the material is chilled in a 100-cc. pyrex beaker surrounded by cracked ice. Seven cc. (not seven grams) of fuming nitric acid (density 1.50) is added in small portions, one drop at a time at first, and the material is stirred over, kneaded, and kept thoroughly mixed at all times by means of a porcelain spatula. The addition of each drop of acid, especially at the beginning of the process, causes an abundance of red fumes, considerable heating, and some spattering. It is recommended that goggles and rubber gloves be worn, and that the operation be carried out in an efficient hood. The heat of the reaction causes the material to assume a plastic condition, and the addition of the acid ought not to be so slow that the material becomes hard. After all of the acid has been added, the dark brown dough-like mass becomes friable on cooling. It is broken up under water with the spatula, rinsed, and allowed to stand in water overnight, then washed thoroughly on the filter and allowed to dry at laboratory temperature. The product is ground up with three and one-half grams of picric acid, made into a moist meal with gum-arabic water, and pelleted. It yields about twenty pellets one cm. long and eight mm. in diameter. These should be allowed to dry for four or five days at room temperature before they are used.

An experiment was carried out in accordance with these directions except that the linseed oil was omitted. The powdered mixture of nitrated naphthol pitch and picric acid, when made into pellets with gum-arabic water and dried, burned with a sooty flame, but did

not give snakes. Another portion of the mixture was made into a sticky meal with linseed oil and compressed into pellets. The pellets, when lighted, started to give snakes but did not maintain their combustion. After they had stood in the laboratory for two months, during which time the linseed oil had oxidized and the pellets hardened, they gave excellent snakes. The conclusion is indicated that oxidized linseed oil is necessary for the formation of the snakes, and that this component of the mixture is conveniently assured by mixing linseed oil with the naphthol pitch before nitration.

Since naphthol pitch is not easily procurable, some other material was sought—some common laboratory chemical from which a chemist may easily prepare black snakes for his own amusement or for the edification of students. Anthracene was tried with the thought that the rather violent nitration is accompanied by oxidation, which perhaps may result in the linking together of a number of aromatic nuclei, to form a material predisposed toward the production of a carbonaceous residue—but the product melted in the flame, gave no snakes, and did not maintain its combustion. Technical  $\beta$ -naphthol was found to be satisfactory. When the procedure described above was tried with ten grams of technical  $\beta$ -naphthol instead of ten grams of naphthol pitch, seven cc. of fuming nitric acid (density 1.50), and so forth, the pellets gave good snakes, thicker than those from the naphthol pitch but not so long, not so shiny, blacker, and covered with wart-like protuberances or having a segmented appearance. A similar experiment with  $\beta$ -naphthol and seven cc. of ordinary c.p. nitric acid (density 1.42) gave better snakes, somewhat longer and smoother than those from the experiment in which fuming nitric acid was used, but still not as good as those from naphthol pitch. The snakes from  $\beta$ -naphthol, however, are perfectly good, and will probably be satisfactory if none from naphthol pitch are available for comparison.

---