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AN HISTORICAL ACCOUNT OF PHARAOH'S SERPENTS

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Almost a hundred and twenty years ago, Porret [1] described the preparation of a new "red tinging acid" which formed with protoxide of mercury an insoluble white salt which he called "sulphuretted chyazate of mercury."

An aqueous solution of this acid—thiocyanic acid—was later prepared by Berzelius [2] by distilling ammonium thiocyanate with concentrated sulphuric acid. Since cyanogen $(CN)_2$ had recently been obtained by Gay Lussac [3] by heating mercuric cyanide, Berzelius naturally hoped to obtain thiocyanogen $(CNS)_2$ by the action of heat upon the mercury thiocyanate prepared by neutralising the parent acid with mercuric oxide. His expectations were not, however, realised,[1] for carbon disulphide and nitrogen were evolved and cinnabar sublimed. Distilled with one-third of its weight of sulphur, however, the salt decomposed violently, forming carbon disulphide, cyanogen and nitrogen, and a black, porous, pumice-like mass was formed in such abundance that the apparatus was broken open.

In the same year, Wöhler [4] attempted to prepare anhydrous thiocyanic acid by the action of sulphuretted hydrogen upon mercury thiocyanate, and was actually the first to record the very characteristic snake-like development of the residue [2] formed when this salt is allowed to burn in the air. He writes: "Erhitz man es gelinde, so schwillt es plötzlich, sich gleichsam aus sich selbst in wurmartigen Gestalten windend, um das Vielfach seines vorigen Umfangs auf. . . ."

[1] Thiocyanogen was not obtained until 1919 when Söderbäck prepared it by the action of bromine upon lead thiocyanate. It forms colourless crystals m.p. — 2 to — 3° C.

[2] This amorphous residue "mellon" formed the subject of numerous researches by Liebig, Gerhardt, etc. The originally proposed formula C_3N_4 was later amended to $C_6H_3N_9$ but its constitution has not yet been thoroughly established. Cf. Franklin, *J.A.C.S.*, 1922, **44**, 506.

Wöhler's mercury thiocyanate was certainly not a pure compound for his method of preparing it " durch Vermischung einer Auflösung von Schwefel-Cyankalium mit der Auflösung von saltpetersaurem Quecksilber Oxydul " was shown by Hermes [5] to yield not mercurous thiocyanate, but a mixture of mercuric thiocyanate and metallic mercury which is much less combustible than the pure mercuric salt which is readily ignited by a match.

The existence of mercurous thiocyanate was, indeed, for a long time a matter of controversy (cf. Hermes [6]) until Phillips [7] described the conditions essential to its formation. The latter points out that although the mercurous salt swells up like the mercuric salt on heating, the residue does not develop the same snake-like convolutions. It is of interest to note that the compounds HgCl(SCN) and HgBr(SCN) also intumesce on heating [8], whilst the selenium compounds $Hg_2(SeCN)_2$ and $Hg(SeCN)_2$ behave exactly like their sulphur analogues [9].

More than forty years elapsed before the commercial possibilities of Wöhler's interesting observation were realised by one Barnett and we then read of a new conjuring trick exhibited in Paris in 1865 in which the magical materialisation of " serpents de Pharaon " was undoubtedly to be attributed to small pellets of mercuric thiocyanate which thus appeared for the first time under this now familiar synonym [10].

On the Continent the new playthings rapidly became popular and they appeared simultaneously in Germany as " Pharaoschlangen " or " Riesenschlangen " and in Italy as " serpenti Indiani." In England, Fred Tolhausen [11] sealed a Patent in March 1866 for the manufacture of a " firework composed . . . of sulphocyanate of mercury."

However much one may admire the commercial acumen which so ingeniously described the tiny pellets of mercury thiocyanate as " Pharaoh's Serpents " eggs, one feels bound to deplore that felicity of description is not here wedded to an equally exact display of erudition. For though in Exodus [12] we read that Aaron " cast down his rod before Pharaoh . . . and it became a serpent," and that the magicians of Egypt " also did in like manner with their enchantments. For they cast down every man his rod, and they became serpents : but Aaron's rod swallowed up their rods," it is clear that these serpents had nothing pyrogenic in their origin or behaviour.

Furthermore, the " fiery serpents " of Numbers [13] which " bit the people : and much people of Israel died " had equally no relation to Pharaoh, and indeed harassed the Israelites at a

time when their vicissitudes under his rule could have been little more than a memory.

In view perhaps of such inconsistencies, Eulenberg [14] adopts the description "Phanarschlangen," deriving this from the Greek *φαναριον* (*i.e.* little flames, or lights): this derivation, however, if not due solely to some typographical error or another, can scarcely be regarded as anything more than a philological *jeu d'esprit.*

In 1882, H. Fleck [15] designated tiny pellets of mercuric thiocyanate as "Hinterladen" (*i.e.* breech-loaders), referring doubtless to the contemporary scatological humour which applauded their insertion, prior to their ignition, in the manner of a suppository[1] into the anus of a grotesque porcelain miniature (*choleramännchen*).

A recrudescence of this essentially Teutonic humour appears at intervals in this country in the guise of porcelain Chinamen which develop abundant black pig-tails, or, less delicately, of china pigs from which sprout phenomenally long and curly tails.

The poisonous properties of Pharaoh's Serpents were soon discovered, for the manufactured articles which consisted of cone-shaped fragments of the mercury salt wrapped in silver paper (tin-foil) were easily confused with a sweetmeat or bon-bon. "Prince O." is said to have very narrowly escaped death as a result of such a mistake [16], and his indiscriminate gourmandising certainly had a fatal effect upon an intestinal tape-worm which he harboured.

Since up to 1904 no actual deaths had resulted in Germany from the internal administration of mercuric thiocyanate, and but few cases of poisoning with serious or fatal consequences had been reported from elsewhere, the practical efficiency of the antidotes proposed by Helbig [17] and Th. Husemann [18] has not been adequately tested.

In order to promote their steady combustion it became customary for the manufacturer of Pharaoh's Serpents to add some 2 per cent. of potassium chlorate or nitrate. This certainly tended to increase the amount of free mercury vapour and was therefore discountenanced by many authorities [19].

On the other hand, Fleck [15] showed experimentally that during the combustion of one serpent's egg in a room, a process which occupied a minute, a negligible quantity only (0·00038 g.) of mercury

[1] *Suppository:* a medicated capsule of gelatine, etc., which when introduced into the anus or vagina melts therein and releases the medicaments (*e.g.* oil of theobroma, phenols, morphine, quinine) contained in it. Suppositories are used nowadays in cases of acute constipation, for treatment of vaginal and uterine disorders and in contraceptive practice.

vapour was inhaled. Husemann [20] confirms this opinion and avers that, in such concentrations, the gaseous products of the combustion become dangerous only to those whose personal idiosyncrasies render them peculiarly sensitive to mercurial poisoning.[1]

On account of the more imagined than real dangers of poisoning arising from the combustion of Pharaoh's Serpents, substitutes have from time to time been proposed.

Thus a mixture of potassium bichromate (2 parts), potassium nitrate (1 part), and white sugar (3 parts) was described in 1871 by Dr. Puscher [21], and Dr. Bersch recommends a mixture of ammonium bichromate (1 part), sugar (2 parts), potassium nitrate (1 part) and enough Peru balsam to yield a plastic mass.

Quite an elaborate substitute is described by Donath [22]. Cigar ash heaped up in the form of a cone is covered with three or four Emser Pastilles,[2] soaked in spirit, and ignited. The mound burns like a wick and just as the flame is about to go out " an adventurous serpent, corpulent and revolting, crawls out from the ash . . ." According to Helbig [17], the expensive Emser Pastilles may be replaced by a mixture of sodium bicarbonate (0·1 g.), sugar (0·9 g.), and tragacanth (0·03 g.).

The most, and perhaps the only effective substitute, and one which has been extensively adopted by the Trade, was first described by Vorbringer [23] so long ago as 1867. It consists of a resinous material obtained by the action of fuming nitric acid upon certain by-products of coal-tar distillation which, when ignited, exhibits " in hohem Grade die Eigenschaft des Rhodanquecksilbers, sich in seinem Volumen bedeutend zu vergrößern. Ein Kegel von 1″ Länge eine Schlange von 4′ lieferte." The preparation of this material is discussed by Vanino [24] and Musprat [25].

Pharaoh's Serpents appear to be perennially popular and a comparison of the earliest recorded analyses [10] with those of Dr. Vanino in 1904 [24] and with some analyses carried out by the author upon various contemporary specimens of " Snakes in the Grass," etc., reveal but little evidence of evolutionary tendencies among these Reptilia.

The modern " eggs " exhibit perhaps a more elaborate structure. In some, a foundation of sodium bicarbonate and sugar is overlaid with a resinous material which has the properties described by

[1] Cf. Stock, *The Hydrides of Boron and Silicon*, Cornell University Press, 1933, pp. 19, 203 f.

[2] Emser Salz, consisting essentially of sodium chlorate (1 part) and sodium bicarbonate (2 parts), takes its name from the hot alkaline springs of Ems, a German Spa near Coblenz.

Vorbringer, and the top of the cone is furnished with a mixture of picric acid and aluminium powder. In others, an inner cone of mercuric thiocyanate, admixed with a small amount of potassium chlorate, is overlaid with a layer of ammonium bichromate which furnishes the " grass " from which the " snake " subsequently creeps. This combination is by far the most effective. Following the prescription of Böttger [26], a spotted or a jet-black snake may be made by impregnating the mercury salt with an alcoholic solution of shellac, or dammar-resin respectively.

REFERENCES

1. *Phil. trans.*, 1914, 527.
2. *Schweiggers Journal*, 1821, **31**, 56.
3. *Gilberts' Annalen*, 1816, **53**, 139.
4. *Gilberts' Annalen*, 1821, **69**, 272.
5. *Journ. pr. Chem.*, 1866, **97**, 477.
6. *Ibid.*, pp. 465 *et. seq.*
7. *Poggendorfs' Annalen*, 1867, **131**, 89; *Zeit. Chem.*, 1867 (2), **3**, 553.
8. *Gmelin-Kraut*, 7th ed., Vol. V, pp. 872, 874.
9. *Ibid.*, p. 868.
10. *Chemical News*, 1865, **12**, 158; Wood, *ibid.*, p. 170; Carpenter, *ibid.*, p. 307.
11. *Chem. News*, 1866, **14**, 69.
12. Exodus, Chap. vii., verses 10–12.
13. Numbers, Chap. xxi., verses 6–9.
14. *Real Encyklopädie der gesamten Medicin*, 3rd ed., 1898, **18**, 605.
15. *Jahrsbericht der k. chemischen Centralstelle*, Dresden, 1882, pp. 27 *et seq.*
16. *Chem. News*, 1865, **12**, 158.
17. *Pharm. Centralhalle*, 1904, **45**, 52.
18. *Handbuch der Therapie innerer Krankheiten*, by F. Pentzoldt and R. Stintzing, 2nd ed., Vol. II, p. 432 (Jena, 1897).
19. Brimmeyr, *Dinglers' polytechn. Journ.*, 1865, **178**, 469.
20. *Real Encyklopädie der gesamten Medicin*, 3rd ed., Vol. V, p. 242.
21. *Chem. News*, 1871, **23**, 215.
22. *Physikalisches Spielbuch für die Jugend*, Brunswick, 1902.
23. *J. pr. Chem.*, 1867, **102**, 187.
24. *Pharm. Centralhalle*, 1904, **45**, 238.
25. *Encyklopädisches Handbuch der technischen Chemie*, Vol. VII, p. 615.
26. *Pharm. Centralhalle*, 1866, **7**, 123; *Dinglers' polytechn. Journ.*, **179**, 163.