

The Manufacture of Calomel in Japan.

By

Edward Divers, M. D., F. R. S., *Prof.*

Imperial University.

(With Plates I-III)

Introductory.—Calomel, in the form common in England and all countries under Western civilisation, is now extensively used and is even manufactured in Japan, under the name of *kankō*. But mercurous chloride is also largely used here, under the name of ‘light powder,’ *keifun* (Chinese, *kingfun*), in another and very much older form, which is of signal purity, and made by a simple process as yet quite unknown in Europe. I witnessed this interesting process from beginning to end some years ago, and now make this publication of it with full permission of the proprietor of the works I visited, Mr. H. Kokubu, who has aided me in every way he could, and notably with drawings, some of which illustrate this paper.

Historical.—According to Terajima Hōkyō and Ono Ranzan, writers who lived in the last century, the first-named perhaps a little earlier, calomel was known in Japan as far back, at least, as the beginning of the eighth century, having then been presented to the Empress Gen-miyō ; but their authority is the *Zoku Nihongi*, reference to which, Professor Haga, F.C.S., informs me, makes it clear that mercury itself, not its chloride, was the thing presented. In the time of the writers above named, mercurous chloride was well-known and

was manufactured in Japan, not only at Isawa, a village in Isé, where it is still made, but also in the city of Osaka and in a town near it, called Sakai. Mr. H. Kokubu, manufacturer, tells me that records exist at Isawa-mura of his family having carried on the manufacture of *keifun* there for the last three hundred years.

Far earlier, namely, in the tenth century Minamoto-no-Shitagō, in his work entitled *Wamyō-Eiijūshō*, makes mention of a mercurial preparation named *kōfun* or 'powder of mercury.' It is, however, questionable whether this was mercurous chloride or mercuric oxide, and therefore whether calomel was known or not at this time. But since calomel, under the name of *keifun*, is mentioned by Chinese writers even earlier than this it may be safely accepted that Japanese knowledge of this body is older than that in Europe. The Western knowledge of chloride of mercury dates from the first half of the sixteenth century, but the distinction between calomel and corrosive sublimate was not recognised till near the end of that century.

Literary.—The literature on Japanese calomel is meagre. Japanese writers of the old school have contented themselves for the most part with translating Chinese writings. Ono Ranzan mentions that the Japanese method differs from the Chinese in making use of water in place of alum and other chemicals, in which he came near the truth. The late Dr. Geertz, who in the Government service did much in establishing Western pharmacy in Japan, treated of *keifun* in some metallurgical contributions he made to the *Transactions of the Asiatic Society of Japan*. What he wrote is contained in vol. iv (1875), and consists of information almost exclusively about Chinese calomel, and gained more from Chinese and Japanese writings than from any experience of his own. Concerning Chinese calomel English readers have the *Notes on Chinese Materia Medica*, among the *Science Papers* by the late Daniel Hanbury, F.R.S., edited by J. Ince. Hanbury

mentions, as the result of his own observation, the characters of *keifun* and its great purity but for the presence of minute, transparent, acicular crystals of calcium sulphate. He refers to Porter Smith's *Contributions towards the Materia Medica and Natural History of China* for an account of the manufacture. Smith, however, takes his information solely from Pearson's account on p. 59, vol. iii of Sir J. Davis's work *on the Chinese*. I have not seen this book, but it is clear from Porter Smith that Pearson, again, has only derived his information from the Chinese *Materia Medica*, *Pun-tsaou-kang-muh*, and not from his own observation, and it amounts to this :—Common salt and mercury, of each one oz.; alum, 2 ozs.; or, salt, mercury, copperas, and saltpetre, in some such proportions ; are rubbed together and put into an iron bowl which is then covered with a roomy earthen dish well luted down. This is exposed to the heat of a strong charcoal fire for four or five hours, when water is thrown on the cover and the cover taken off. On its inner surface the calomel is found adhering in the form of a beautiful, feathery, white sublimate. Ten parts of mercury are said to yield about eight parts of calomel. Dr. Geertz's paper, already referred to, contains essentially the same account translated from the Japanese version of the Chinese work.

Lastly, there is a paper, in the Japanese language, on the manufacture of *keifun* at Isé, which is the forerunner of the present one. That paper appeared in 1887 in the *Journal of the Tōkyō Chemical Society*, by Mr. T. Shimidzu, M.E., F.C.S., my former pupil and colleague, and it was his description to me of what he had seen that led to my own visit to Isé in company with Professor Haga in the following year. In one or two points I have availed myself of this paper to make my own account more complete.

Of the specific properties of keifun.—*Keifun* is in very thin minute scales, lustrous, transparent, and white or faintly cream-

coloured. It might be described as micaceous calomel. To the touch it is soft and smooth. Measured in bulk, dry, it is four times as voluminous, more or less, as the ground calomel prepared by the European process, and can be readily scattered by a puff of the breath. Rubbed hard in a porcelain mortar it gives the brown resinous streak characteristic of calomel and the evidence therefore, according to pharmaceutical authorities, of its freedom from corrosive sublimate. Exposed to bright sun-light it gradually assumes a light brown colour, a colour, that is, having no affinity to grey or black. Moisture does not seem to favour this change which is certainly not owing to any reduction to metal. European calomel suffers a similar change. *Keifun* is free from corrosive sublimate, and from metallic mercury.

Hanbury found selenite in Chinese calomel, and Geertz found calomel of this form generally adulterated with selenite and mica, but whether what he examined was ever Japanese and not always imported Chinese calomel he does not show. I have found *keifun*, as it came direct from Isé, quite free from adulteration, and have not met with any adulterated.

Of the material used in making calomel in Isé, Japan.—The materials for making Japanese calomel are—mercury, an arenaceous red clayey earth, bay-salt, bittern or salt-mothers, and air. The mercury is imported from Europe, but in old times is said to have been found in the neighbourhood of Isé as cinnabar.

The earth, called *mitsuchi* ('seed-earth'), is all taken from a neighbouring hill, Shunakayama, and according to Mr. Kokubu, many other clays have been tried in place of it, always with bad results. It is of a rather light bright red colour, which changes to a duller and somewhat brown red on drying and gently heating the earth, and to a light ordinary brick red by a strong heat. As mined,

the earth is seen to consist largely of colourless quartz grains. Besides the quartz a very little biotite is seen sparkling through it. The fresh damp earth does not form a compact mass, but a slightly cohering aggregate of damp crumbs. This texture appears to be due to the earth being a mass of quartz in small grains from the size of a hemp seed down to that of impalpable particles, held together by plastic clay. For use that which does not contain coarse quartz grains too abundantly is selected, and is made into briquettes and moderately baked on the hearth of the fire-place under the calomel pots. These briquettes are then as light and porous as the prepared porous clay used in Fletcher's gas-furnaces. The raw earth air-dried is readily rubbed into its constituents by the fingers; and the baked briquettes very easily and rapidly reduce to a soft powder, quartz grains and all, in the agate mortar. The larger grains of quartz in the raw earth are also very brittle. I have treated thus fully of the mechanical characters of the earth, because probably much of its efficiency is due to them. But its chemical character also calls for notice. As baked ready for use it contains in the thoroughly air-dry condition still 5 per cent. and more of water. Before ignition it is almost entirely decomposed by sulphuric acid, either in some days in the cold or quickly by heat. It is also largely acted upon by hot hydrochloric acid, and heated in sealed tubes with this acid to 120-150°, it is almost as fully decomposed as by sulphuric acid. It contains practically no silica soluble in hot sodium-carbonate solution, but after acid treatment yields, of course, much silica to this reagent. The composition of the earth, as found in use at the works, but rendered anhydrous is as follows:—

Quartz	38.4
Combined silica	24.2
Alumina	26.3
Ferric oxide... ..	10.5
Magnesia	0.2
	<hr/>
	99.7
	<hr/>

The magnesia is only got by fusion of the finely ground earth with alkali carbonate, and belongs to the particles of mica scattered, through it. Only doubtful traces of phosphoric acid could be found and, what is specially to be noted, no lime whatever. The earth is thus nothing but quartz, kaolin, ferric hydroxide, and a very little biotite, and is probably valuable to the calomel maker not only for its highly porous texture, but also for its negative chemical qualities.

The bittern and even the rough bay-salt contain magnesium chloride, and this rather than sodium chloride must be the source of hydrochloric acid in the process. That air finds a graduated entrance to the other materials by diffusion during the process, will become evident from a consideration of the set-up of the apparatus.

Of the plant.—The apparatus for making Japanese calomel consists of a table-furnace supporting sixty cast-iron pots lined and surmounted with the Shunakayama earth, on which rest, as covers, and condensers and receivers of the calomel, unglazed clay cups bottom upwards. In Pl. I. the furnace as it is when in action is seen from the working side; ten pots on the left side are shown still to be charged and covered. The wooden step in front is to enable the workman to reach over the table easily when charging the pots or emptying them. In Pl. II, fig. 1 the furnace is seen from the back, or firing side, and with the walls broken away to show its interior and the method of firing. In Pl. II, fig. 2 the mounting of the pots is shown in three stages by sectional plans of the table.

On a smoothed clay hearth the walls of the furnace are raised in clay, building, in the three stones which frame the stoke hole (Fig. 2). The walls are 2.6 ft. high and the enclosure is 7.6 ft. by 4.7 ft. measured outside. The stoke hole is 1 ft. by 1 ft., but a little wider than this at the base, and is without door. The table of pots and roof of the furnace is constructed (Pl. I and Pl. II, fig. 2) by laying a square iron rod on each of the long walls, and on these eleven cross rods also square on which are to rest the flanges of the pots. The pots are then put in position as close together as possible, hanging by their flanges, in ten rows of six each, and plastic clay pressed into the openings left between the flanges and the rods, and the rods and flanges covered in so that only the mouths of the pots remain visible, as shown by the middle rows in Fig. 2. The furnace clay being thoroughly dry, it is deeply laid over with the red earth mixed with a little bay salt and moistened with bittern in small quantity. The pots are also filled with the same moist red earth, except a central cylindrical shaft (see the left side of the furnace-table in Pl. I or the right side in Pl. II, fig. 2) reaching to the bottom of the pot, which is left bare. The pot is 0.5 ft. deep inside, and across its mouth, inside, is 0.45 ft. It is shown in Pl. III, fig. 4. The shaft or cavity left in the filling is 0.18 ft. in diameter, and is shaped by resting a wooden core on the bottom of the empty pot, and then pressing-in the moist earth round it, smoothing-off the top, and dropping a perforated board over the projecting core to hold down the earth while withdrawing the core which is then removed by its handle. The furnace is now ready for work. It should have been mentioned that after the clay walls of the furnace are built they are framed-in with wood to increase their stability and to give support to a wooden back and to shelving above the table, as seen in Pl. I.

Of the firing.—The firing the pots is kept far below what are

usually regarded as furnace heats. The fuel employed is wood, and the Japanese are certainly clever in the use of this, in the old style of furnaces, economically and effectively in firing pots for boiling, evaporating, distilling, or subliming. The method of heating is seen in Pl. II, fig. 1. Five lengths of fire-wood are ranged along the back and front walls on the hearth, generally raised at one end by resting on a lump of clay. In the ordinary working of the furnace, as I saw it, the heat from previous work is sufficient to kindle the fresh wood. The flames rise up the sides and run over the bottoms of the pots, leaving the central space in the chamber free from flame. The air enters by the lower part of the stoke hole and the products of combustion escape, invisible, by its upper part, so perfect is the combustion. At the time of first lighting the fire and of irregularities in stoking, some smoke is unavoidable, and to keep the top and table free from this smoke and from ashes, a wooden back is put in above the table as shown in the figures. There is also a wooden hood and flue above the stoke hole, to carry off any smoke; this is not shown in the figures, but is similar to those put up in England and elsewhere, over the working doors of furnaces to protect the workmen from arsenic, sulphur, or other noxious fumes. The heating is so well effected that the pots two feet above the burning logs are made sufficiently hot, barely red-hot at the bottom, and yet the wooden frame on the outside of the furnace is not charred, and the work-room is not unpleasantly warmed. About three bundles or 40 lbs. of wood serve for one firing, and it is remarkable to see so little fuel working so many pots.

Of the working.—A compost of burnt *mitsuchi* with about a fourth of its weight of bay salt is made up with bittern into lumps the size of large chestnuts. The furnace being hot enough, the *mitsuchi* surface of the table is once for all freely wetted by a watering-pot, perhaps half a

gallon of water being used, all of which is absorbed ; a lump or two of compost is dropped by tongs or by hand into each pot in rapid succession ; a very small spoonful of mercury poured into each pot, the total charge for the sixty pots being somewhat less than one pound avoirdupois, (more exactly $\frac{5}{8}$ of a lb.), and a clay cup, bottom up, placed over each pot and adjusted by gently pressing, and turning it round slightly. The cup is thus made to fit neatly on the earthen top without adhering to it in the least. The cups are thick and unglazed, but become very smooth inside by use. They have an inside diameter at the mouth of 0.5 ft. and a depth of 0.25 ft.

Thus arranged, the pots and cups are left for three hours, and during the latter part of this time the furnace is cooling. When cool enough, each cup is lifted in turn, and, with two turns of a feather, the *keifun* or calomel, which fills it in the form of a sparkling network of delicate crystalline scales, is transferred to a sheet of paper held under it, and the cup, mouth downwards, placed on a shelf of the furnace ready for use in the next operation.

The calomel, it will thus be seen, forms no adherent cake in the cup, but particles only loosely hanging together. So obtained it is ready for the market, needing only to be packed in small wooden boxes for sale.

The spent lumps of earth and salt are lifted out of the pots by the tool shown in Pl. III, fig. 5, and when the furnace has become still cooler, the fire is made up again, the furnace top freely wetted, and a new operation set going as before. The furnace is worked twice each day. Nothing could well be carried out with greater simplicity and less expenditure of labour, time, and fuel.

Of the yield.—The loss I am told is about sixteen per cent. of the theoretical amount of calomel which is, I believe, about twice as much as is lost in the Western process.

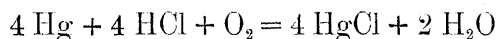
Experimental.—If one of the cups is removed a few minutes after the operation has been started, much of the mercury is found in it as a sublimate of fine globules, mixed with only a little almost amorphous calomel, from which it would appear that the formation of the calomel results from reaction in the cup between the mercury in vapour and the active gases.

On dipping into the pot, uncovered during the process, a glass rod with a drop of water hanging to it and then withdrawing it and testing the remainder of the water with potassium iodide and starch no chlorine can thus be detected. The same is true when a drop of solution of potassium hydroxide is used. Nor can the slightest odour of chlorine be detected in the vapours issuing from the uncovered pot.

On passing air containing a little hydrochloric acid gas through a tube in which mercury is freely boiling, sparkling calomel is formed close to and mixed up with the mercury.

Red earth which has been used in the process turns moist red litmus-paper blue, while fresh red earth is neutral.

Theoretical.—The nature of the materials used and the observations gained by the preceding experiments are sufficient to establish that the calomel is formed by a reaction between mercury vapour, oxygen, and hydrochloric acid gas, in which along with mercurous chloride, water is formed :—



and that the formation takes place at a temperature near—above or below—the boiling point of mercury and much below that at which calomel freely volatilises. The source of the hydrochloric acid is certainly the magnesium chloride of the bittern and bay salt, which heated in a moist atmosphere, even in the presence of sodium chloride,

is, as is well known, partly converted into magnesia and hydrochloric acid. Hence the alkalinity of used *mitsuchi*.

The porosity of the walls of the apparatus particularly of the layer of *mitsuchi* on which the clay cup rests, must be more than sufficient to allow enough air to enter during the working. I had supposed that the hot hydrochloric acid and air might, in contact with the earth, have yielded a little chlorine, but the temperature reached in the process, normally worked, seems never to reach that required for the liberation of chlorine.

The Chinese process, if *correctly described*, differs from that used in Japan in several material points, one of which is that the mercury is intimately ground up with the other materials, and one fails to see what reaction can take place between it and the two others, namely, salt and alum. Heated, the mixture must give off mercury and hydrochloric acid, and then these as in the Japanese process will with air give the calomel ; but this is independent of the previous intimate mixture of the mercury with the salt and the alum. Another point is that in place of the magnesium chloride of sea-water as the source of hydrochloric acid, the Chinese are said to use alum, or copperas, which with the salt will react to give hydrochloric acid. A third point is that the cover is said to be closely luted to the iron pot, which must nearly exclude the air, without which it is impossible to explain the formation of the calomel. Perhaps this is the reason why the Chinese process is said to take four or five hours firing, since this may give time enough for the needed oxygen to diffuse through the cup and luting : it will also account for the fact, if it is one, that the yield of calomel is markedly less in weight than the mercury used. Again, there are to be noticed the statements that the iron pot is exposed for hours to the strong heat of a charcoal fire, and that the hot clay cover is cooled by throwing cold water on it, statements which must be

regarded as greatly exaggerated, if not erroneous. Lastly, the calomel-giving vapours are allowed to remain in contact with the hot iron of the pot instead of being kept from it by the thick lining of earth provided in the Japanese process, a contact which such vapours could not stand without destruction. I think, therefore, that we may be fairly doubtful whether any reliable description has yet been given concerning the Chinese process, which we may expect to find to differ little, if at all, from the Japanese process, except in salt and alum being used in place of the mother-liquor of sea-salt, or 'water' as Ono Ranzan supposed it to be.


One thing, to which attention may be called, is that the Chinese are stated to add some nitre to a similar mixture when employed to give corrosive sublimate. For that being the case, it is seen that free chlorine, which would here be developed from the salt, nitre, and alum, is necessary for the production of the higher chloride, and that air and hydrochloric acid can only yield the lower chloride, a difference of much theoretical interest, and indeed of practical moment also.

It is known that re-sublimation of calomel generates some corrosive sublimate, and, although authorities are not quite agreed as to whether reaction occurs between gold leaf and calomel vapour, it is hardly to be doubted that such reaction does occur. Now I have found that if in the Japanese apparatus the temperature of the cover is raised sufficiently to volatilise much of the calomel, the remaining calomel is no longer free from corrosive sublimate. It must therefore be borne in mind that the calomel formed in the Japanese process is not, and cannot be, the result of true sublimation, but of precipitation as fast as formed from the three gaseous bodies which give rise to it. At the temperature at which mercury boils, calomel is either quite fixed or at most has a vapour of exceedingly small tension. In the two facts, that the three gases do not react to yield corrosive sublimate

and that the calomel is not heated to its volatilising point, lie the explanation and, at the same time, the assurance, that Japanese (and Chinese) calomel contains no corrosive sublimate.

Summary.—The Japanese prepare calomel pure, above all things free from corrosive sublimate. They heat balls of porous earth and salt, soaked in bittern, along with mercury, in iron pots lined with earth. The heat forms hydrochloric acid from the magnesium chloride in the bittern, and the mercury sublimes into the closely-fitting but unattached clay covers of the pots. Air enters by diffusion, and oxygen and hydrochloric acid gas act together in the hollow cover on the vapour given off from the sublimate of mercury there formed. The cover thus becomes filled with a network of micaceous particles of calomel, precipitated, at a temperature below its subliming point, at the moment of its formation.

This investigation of an interesting product of Japanese industry has been carried out under the authority of the Imperial University of Japan. I cannot acknowledge fully enough the indispensable assistance I have received from my colleague, Assistant-Professor Haga, F.C.S.



Description of Pl. III.

- Fig. 1. Tongs for lifting and dropping the lumps of wet compost into the pots.
,, 2. Brass mercury spoon.
,, 3. Clay cup condenser.
,, 4. Iron furnace-pot.
,, 5. Peel for lifting compost ball out of pot.
,, 6. Quill feather for emptying cups.
,, 7. Wooden water-pot, for wetting furnace top.
,, 8. Wooden core and board for lining pots.
,, 9. Rectangular iron bars for pots.

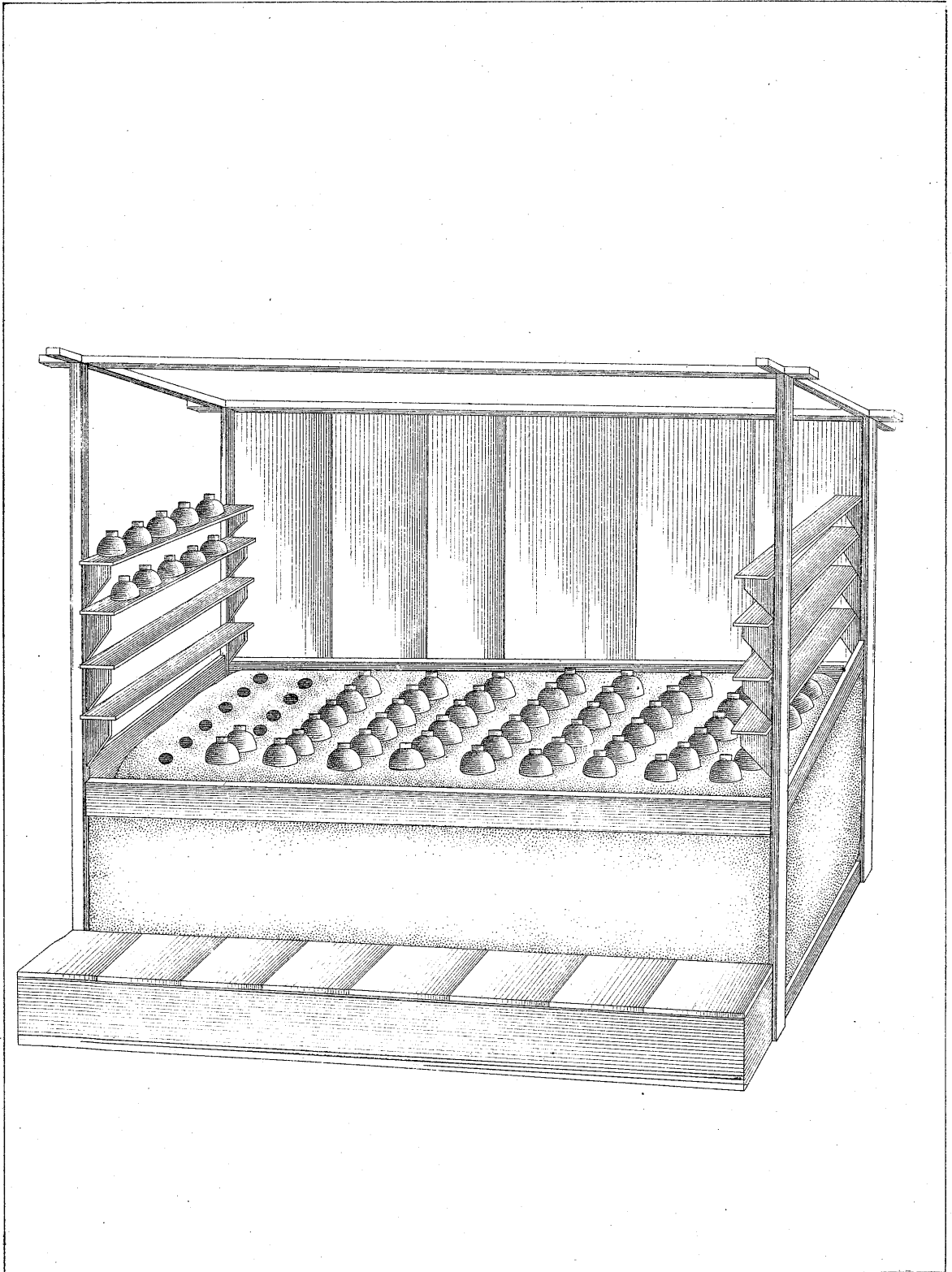


Fig. 1.

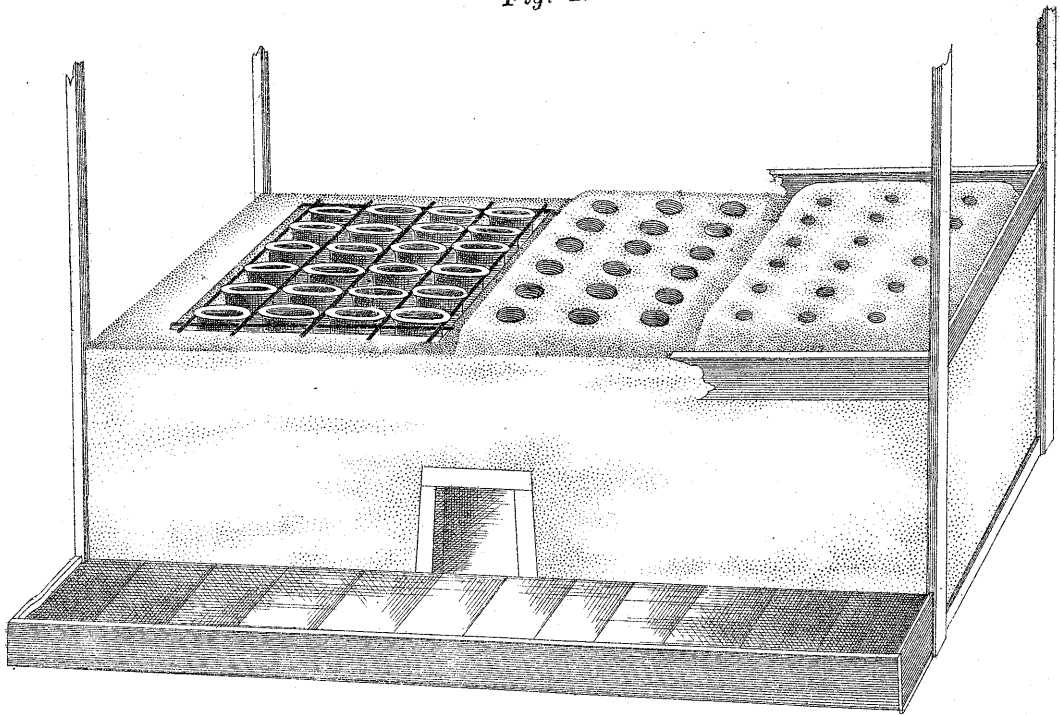


Fig. 2.

