Cl. 167

Published May 11, 1943

Serial No. 254,967

ALIEN PROPERTY CUSTODIAN

PROCESS FOR MAKING FROTHS CONTAINING HYDROCYANIC ACID

Leo Löwenstein, Berlin-Wilmersdorf, Germany; vested in the Alien Property Custodian

No Drawing. Application filed February 6, 1939

Hydrocyanic acid is used in large quantities for combating agricultural pests and is employed for this purpose in various forms. In most cases it is used as gas, either out of bottles or by production from chemicals at the place of use. The plants on which it acts must either be in closed spaces or they must be covered by tent awnings in order to keep the hydrocyanic acid gas near to the articles being gas-treated for a sufficient time. Liquids containing hydrocyanic acid have also already been sprayed on to the plants to be treated with gas. Further froths have already been prepared which contain hydrocyanic acid gas.

The formula put forward by Haber applies to the action of hydrocyanic acid; according to it in the poison action of gases in general the product of gas concentration and time of action is constant. Working will be most economical, therefore, i. e. the smallest possible quantity of hydrocyanic acid will be used, if as little gas as possible is permitted to act for as long a time as possible. Apart from the action in closed spaces, this principle can be followed to only a very limited extent in the case of the above-mentioned methods. The tent awnings do not permit a sufficiently high concentration being maintained for a fairly long time. When spraying with solutions, the gaseous hydrocyanic acid is soon volatilised after the drying. This also is the case if the hydrocyanic acid is brought on to the plants in a foam according to the previous proposals.

If the gas containing hydrocyanic acid is dispersed in known manner in the aqueous solution of a froth-former, the froth breaks down in the open after a short time. This also is the case when the gas is formed chemically in the solution, e. g. by decomposition of bicarbonate by means of substances having acid action.

Applicant has now found that in contradistinction to the known methods gas treatment with hydrocyanic acid can be applied to plants in a particularly efficient, simple, economical and certain manner if the procedure is as follows: The hydrocyanic acid is dissolved in water in the form of calcium cyanide, the water containing a froth-former; such as for example saponin. Air or some other gas is then dispersed in this solution, whereby a froth is formed. Although saponin has been proved to be most advantageous as froth-former, the process can also be carried out with other known froth-formers. It is of course important that no jelly-like or pulpy masses permeated with air bubbles form, but proper froths having a honeycomb-like structure, the wall thickness of the bubbles of which is small in comparison with their diameter. The said diameter also should be as small as possible, i. e. the froth should be as fine-bubbled as possible. It has been found that such froths have the best stability.

As is well known calcium cyanide reacts with water to form hydrocyanic acid and calcium hydroxide. It has been found that the latter immediately lodges in the thin walls of the froth bubbles, as a result of which the froth is greatly strengthened. It was not to be foreseen that the two processes of decomposition of calcium cyanide and distribution of the lime particles in the walls would so act together that this effect is produced.

The calcium cyanide can be introduced as such into the solution to be frothed. It may, however, also be formed in known way in a solution of alkali cyanide and a corresponding quantity of a soluble calcium salt.

The stability of the froth may also be raised by adding additional lime in the form of milk of lime to the solution before the frothing up. It has been found that the added lime particles together with the lime particles forming from the calcium cyanide lodge in the walls of the froth cells. The lime content should be such that, together with the lime forming from the cyanide, it amounts to 2–4% by weight of the froth-forming liquid.

Instead of these lime particles also other small solid particles, such as for example alumina, may be lodged in. However lime particles have proved to be best.

It has further been found that the froth may also be prepared by blowing hydrocyanic acid as gas into the liquid containing the froth-former and milk of lime during the froth formation. A froth then forms containing hydrocyanic acid in the liquid and gaseous phases, and in the wall texture of which the small lime particles are lodged.

The agents found suitable for the stabilisation of fire extinguishing froth may be used for stabilising the froth, such as for example gelatin, glue, starch and so forth.

It has also been found that an addition of calcium chloride is very favourable. This addition has a double effect. On the one hand it has been found that the stability of the froth is very much increased, and in fact far more than by dissolution of any other salt, or the substances such as glue and so forth, proposed in the froth extinguishing art for froth stabilisation. Further, the drying out of the froth is very much

protracted thereby, as a result of which the retention of the hydrocyanic acid in the froth and consequently the action of the acid is very much promoted. An addition of 10% by weight of calcium chloride to the solution is already sufficient to bring about these favourable results.

The mechanical carrying out of the froth formation by dispersing air in the liquid to be frothed is effected in known manner by beating, whisking, injection of air or gas in fine subdivision through filter thimbles and the other methods proposed more particularly for fire extinguishing.

It has been found that after the application of the froth, liquid frequently flows off for some time which contains the active constituents contained in the froth in the same concentration as the froth. As a result the efficiency of the froth is reduced accordingly; further in this way hydrocyanic acid can reach places where it might have a harmful effect. It has now been found, however, that this drawback can be removed by allowing a certain time to elapse between the formation and the application of the froth. This time must be sufficiently long for the froth to give up the surplus liquid. For this purpose, either the froth is allowed to stand for a number of minutes, or the apparatus is so formed that the froth requires a certain time to travel through it to the exit thereof. This for example may be effected by choice of the width of the leading tube or by inserted intermediate reservoirs. During this time the surplus liquid flows off so that the applied froth no longer gives up liquid. The liquid flowing off from the froth is not lost however, as it can be used for forming fresh froth.

It has further been found that for the froth to be suitable for the aforementioned purposes the nature of the production thereof is of essential importance. It has been ascertained that a froth which is made by rapidly moving solid bodies in known manner in the liquid to be frothed, such as happens in the case of whipping, whisking and so forth, is substantially better suited for the said purposes than a froth which is made by means of filter thimbles or according to some other process.

For example, a liquid with 0.5% of saponin, 1.5% of calcium cyanide and lime in suspension yielded on injecting air through a very finely-pored filter thimble a froth weighing 9 grams per 100 ccs. After one hour there were still 3 grams present as froth, and after 75 hours there were still about 1 gram with a volume amounting to about $\frac{1}{10}$th of the original volume.

When on the other hand the froth was produced by whisking, 100 ccs. of the froth weighed 16 grams and after one hour still weighed 12 grams, whilst after 100 hours there were still 5 grams of froth present, having a volume of 80 ccs.

It has further been found that a froth made by means of filter thimbles or in some other way can be so improved by the motion of solid bodies therein, such as for example by whisking, that its quality corresponds to the quality of the froth produced right from the start by the motion of solid bodies, i. e. by whipping, whisking and so forth.

Experiments have shown that froths which have been made in accordance with the foregoing description, and in the case of which round about 1.5% by weight of calcium cyanide and 0.5% by weight of saponin have been added to the liquid, remain maintained for several days in the open on plants of different kinds. It is therefore possible completely to kill off the pests coming into question without doing any damage to the plants. After the froths had acted for several days, even in the case of unfavourable weather, the hydrocyanic acid had completely disappeared. More particularly it was found that these froths penetrate better and more deeply than ordinary aqueous solutions, so that they are therefore particularly suitable for treating barks having deep cracks and crevices.

LEO LÖWENSTEIN.