Calcium Cyanide-"Powdered Hydrocyanic Acid""

A New Product of Manufacture

By F. J. Metzger

AIR REDUCTION Co., INC., NEW YORK, N. Y.

P TO the present date no account has been published reporting calcium cyanide as recovered by evaporation or otherwise, on account of its ready decomposition due to hydrolysis or polymerization.

Prior work along these lines may perhaps best be summarized by quoting the following relevant excerpts from "The Chemistry of Cyanogen Compounds and Their Manufacture and Estimation," by Herbert E. Williams:

CALCIUM CYANIDE is known only in solution. * * * A solution of the salt may be readily prepared by passing hydrocyanic acid into milk of lime and a solution may be thus obtained of 30 to 35 per cent calcium cyanide, but such a solution is exceedingly unstable; it smells strongly of hydrocyanic acid, and cannot be kept unchanged for more than an hour or so. The solution quickly turning brown, and depositing dark brown flocks of azulmic acid and crystals of a sparingly soluble basic evanide of calcium * * cyanide of calcium

A solution of 15 per cent or under of calcium cyanide may be kept if out of air contact for years without change, but a solution of any strength above this figure will rapidly turn brown and decompose in the manner described, the rate of decomposition depending directly on the strength; the stronger the solution the quicker the decomposition. A solution of 20 per cent strength may be kept for a day without discoloration, while a 30 per cent solution turns brown in a few hours * * *

Calcium cyanide does not appear to exist in the dry state, it cannot be obtained by evaporation and crystallization of the aqueous solution * * *

and from Thorpe's "Dictionary of Applied Chemistry," Vol. II (last edition):

CALCIUM CYANIDE has never been prepared in the pure state. An aqueous solution of lime in hydrocyanic acid decomposes completely into its constituents when boiled (Scheele). By evaporating such a solution *in vacuo*, Joannis obtained a crystalline compound, $3CaO.Ca(CN)_2$, $15H_2O$, which decomposed completely in a vacuum, leaving nothing but lime. Drv reactions, at high temperatures, yield calcium cyanamide, but no cyanide.

Work done in the writer's laboratories confirmed the observations of other workers as summarized above.

On consideration of the probable properties which dry alkaline earth cyanides might possess, it seemed logical to suppose that if water could be largely eliminated and a reaction found that would not involve the formation of water, such cyanides might be produced. Among the commercially available compounds, calcium carbide seemed a logical source of calcium. Considering the weakly acid properties of hydrocyanic acid we should expect the reaction

$$CaC_2 + 2HCN \rightarrow Ca(CN)_2 + C_2H_2$$

Or again, if anhydrous hydrocyanic acid should not react on calcium carbide directly, then a slight amount of water should catalyze the reaction and calcium cyanide should result without introducing or forming a deleterious amount of water,

$$\begin{array}{c} \text{CaC}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2\\ \text{Ca}(\text{OH})_2 + 2\text{HCN} \rightleftharpoons \text{Ca}(\text{CN})_2 + 2\text{H}_2\text{O} \end{array}$$

the water being catalytic and the reactions continuing in cycles.

Numerous experiments soon confirmed the latter supposi-

¹ Received January 5, 1926. Presented before the New York Section of the American Chemical Society, New York, N. Y., January 8, 1926.

² Patent applications pending.

tion. Hydrocyanic acid containing a slight amount of water reacts readily with calcium carbide, liberating acetylene and forming calcium cyanide. The reaction proceeds rapidly and smoothly to completion, and is guite similar in this respect to the action of water on carbide. The reaction between anhydrous hydrocyanic acid and fresh carbide is extremely slow.

The speed of the reaction increases with increased amounts of water. However, an excess of water is to be avoided, since it tends to increase the amount of polymerization of the hydrocyanic acid and yield a product with lower cyanogen content. An amount of water equivalent to about 2 per cent (calculated on the weight of the carbide) gives very rapid reaction and yields a product of high cyanogen content, with only slight polymerization.

It appears that the reaction is not exactly in accordance with the equations given above, but rather may be summed up \mathbf{as}

$$CaC_2 + 4HCN \rightarrow Ca(CN)_2.2HCN + C_2H_2$$

or in reality this reaction may be entirely analogous to the formation of calcium bicarbonate-i.e., the compound formed may be $CaH_2(CN)_4$.

Raw Materials

The raw materials used are commercial calcium carbide and liquid hydrocyanic acid containing a slight amount of water as catalyst.

The hydrocyanic acid is made by a nitrogen fixation process,³ which may be briefly outlined as follows:

A mixture of finely divided carbon, soda ash, and about 2 per cent iron as catalyst is fed into the upper end of an inclined re-volving furnace. The temperature is maintained within the furnace in the neighborhood of 1000° C. while nitrogen is passed through the mixture. Discharges of a furnace product containing 30 to 40 per cent sodium cyanide are made at intervals. The furnace product is then ground fine through a ball mill. To this finely ground material there is added the necessary finely divided carbon to make up for that lost in the reaction. There is also added just sufficient water to moisten the material and supply the necessary hydrogen to form hydrocyanic acid in the next operation. The mixture is then spread upon a tray within a specially designed gas-tight generator, and carbon dioxide passed through the mass, the reaction being as follows:

$$2NaCN + CO_2 + H_2O \rightleftharpoons Na_2CO_3 + 2HCN$$

The gases leaving the generator pass through a condenser cooled by brine. In this condenser the hydrocyanic acid is liquefied and withdrawn; the excess carbon dioxide passes on to a storage tank, from which it is drawn to treat a subsequent batch of material. The mass left in the generator is of the proper composition for charge material for the furnaces, except that it contains from 5 to 10 per cent of moisture. This moisture is removed by passing the mixture through a rotary drier, from which it is returned to the furnaces, thus completing the cycle.

Flue gas from the furnaces is scrubbed to obtain carbon dioxide, which is used in the generator operation; the residual nitrogen is that used for fixation in the furnaces.

The mechanism of the formation of cyanides when a mixture of alkali metal compounds and carbon is treated with nitrogen has been the subject of a great deal of discussion over a period of many years. It seems, however, to have been finally cleared up by some very careful and thorough experimental work carried

³ F. J. Metzger, U. S. Patents 1,322,195; 1,385,336; 1,388,586; 1,473,826; and 1,498,637,

out by Guernsey and Sherman⁴ in the Fixed Nitrogen Research Laboratory of the U. S. Department of Agriculture.

These investigators showed conclusively that the reaction proceeds in three stages. In the first stage sodium carbonate is reduced by carbon to form metallic sodium and carbon monoxide.

$$Na_2CO_3 + 2C \rightleftharpoons 2Na + 3CO$$

In the second stage sodium in the vapor phase reacts with carbon to form sodium carbide.

$2Na + 2C \rightleftharpoons Na_2C_2$

In the third stage sodium carbide in the vapor phase adds nitrogen to form sodium cyanide.

$$Na_2C_2 + N_2 \rightleftharpoons 2NaCN$$

The authors show that iron acts as catalyst only in the third reaction.

Manufacture

At the plant of the California Cyanide Company, where calcium cyanide is being manufactured, a vacuum crystallizer has proved well adapted for the purpose. The writer's company is using standard vacuum crystallizers 6 feet in diameter. Each crystallizer is equipped with two gas-tight hoppers, one for feeding the carbide mechanically by means of a worm directly into the crystallizer, the other for the purpose of adding any desired substance to the compound. The vapor and gas line leads from the crystallizer through a surface condenser cooled by brine. These crystallizers take normally a charge of 300 pounds of carbide and yield about 600 pounds of finished product.

The acetylene gas leaving the condenser still contains a small amount of hydrocyanic acid gas and is passed through a scrubber in which dilute alkali is circulated to remove the last traces of hydrocyanic acid.

In making a batch the carbide hopper is charged with 300 pounds of finely ground carbide. A vacuum pump exhausts the air from the system and approximately 900 pounds of pure liquid hydrocyanic acid containing about 6 pounds of water (2 per cent on the weight of carbide) are drawn from a weighing container into the crystallizer. The agitator is started and cold water is circulated through the jacket of the crystallizer. The carbide is fed mechanically from the hopper into the crystallizer at such a rate that the entire 300 pounds are introduced in 1/2 to 3/4 hour. A rapid evolution of acetylene takes place and the entire reaction is completed in $\frac{3}{4}$ hour to 1 hour after the initial introduction of the carbide. At this stage the mixture in the crystallizer is nearly white and resembles ordinary acetylene sludge. Warm water is then substituted for the cold water in the jacket of the crystallizer, agitation is continued, and the excess of hydrocyanic acid evaporated. Slight discoloration of the product takes place as evaporation proceeds, and at the completion of the drying there remains a light, very finely divided powder of light tan color. The material is then discharged from the crystallizer into air-tight containers. The excess hydrocyanic acid which has been evaporated off and condensed is returned for the treatment of a subsequent batch.

When it is desired to add other materials, such as sulfur, arsenate of lead, etc., these substances are added through the second hopper during evaporation of the excess liquid hydrocyanic acid. The total time required to produce a batch as described is from 3 to 4 hours.

Properties

As may be seen from the method of manufacture, the finished product contains only such impurities as are common to calcium carbide, together with the small amount of polymer which is responsible for the color of the compound. It is in an extremely fine state of subdivision and therefore is ad-

4 J. Am. Chem. Soc., 47, 1932 (1925).

mirably adapted for dusting purposes. The cyanogen content will vary somewhat, depending upon the quality of carbide employed in its manufacture and the details of manipulation; it will, however, range between 52 and 58 per cent, averaging about 55 per cent, the latter being equivalent to 103.6 per cent sodium cyanide.

The product is readily soluble in water, evolving a small amount of heat. The water solution gives the characteristic reactions for calcium and cyanogen ions. The product is also readily soluble in ordinary ethyl alcohol and in methanol both in their absolute and dilute forms.

The product is stable when heated to temperatures up to 100° C. It begins to decompose slightly at about 120° C. It remains unchanged when exposed (in air-tight containers) over long periods of time at temperatures ranging from freezing to 60° C. (140° F.).

The product is extremely sensitive to moisture, being decomposed with the liberation of hydrocyanic acid.

$CaH_2 (CN)_4 + 2H_2O \rightarrow Ca(OH)_2 + 4HCN$

The moisture of the air liberates hydrocyanic acid very rapidly, so much so that when spread in extremely thin layers about three-quarters of the hydrocyanic acid content has been evolved in half a minute and practically all of it in one minute. Such evolution of gas takes place on exposure to air even when the humidity is 25 per cent or less. The reaction with atmospheric moisture is so rapid that the evolved gas may be readily ignited.

Uses

From the properties just described it is obvious that calcium cyanide is particularly suitable for such operations as have hitherto been accomplished by means of liquid or gaseous hydrocyanic acid. Its extremely fine state of subdivision makes distribution of the gas a simple operation. The product has many advantages over liquid hydrocyanic acid, notably in its safety in handling, transportation, and application. The powder is perfectly stable under all ordinary conditions of storage and transportation, provided only that it be protected from atmospheric contact. On the contrary, liquid hydrocyanic acid is dangerous to handle, and it is difficult and dangerous to transport since it is subject to spontaneous polymerization which may result in violent explosions. Since mere exposure to the air liberates hydrocyanic acid freely and practically quantitatively from calcium cyanide in a very short time, this new product has been called "powdered hydrocyanic acid."

The citrus industry struggles constantly against a pest known generally as scale. Hydrocyanic acid gas obtained in various ways has been used for combating this pest for many years. The common practice at present is the application of liquid hydrocyanic acid under tents placed over the trees. The industry is, however, confronted with the fact that there is a comparatively narrow margin between the dosage which controls the scale and that which injures the fruit or tree or both. It has long been known, also, that the ranges of toxicity of liquid hydrocyanic acid for plant and animal life approach coincidence much more quickly in daylight than in darkness; the same applies to damp or foggy atmospheric conditions. Hence, in practice, such fumigation is carried out at night in comparatively dry weather. When calcium cyanide is used for fumigation-as, for instance, by dusting it under the fumigating tents-field experiments have demonstrated that a satisfactory kill of the scale, without injury to fruit or tree, can be secured by the application of much less total cyanogen than would be contained in the liquid hydrocyanic acid dosages which have been established as standard by scientific experiment as well as by years of practical experience. Field work has demonstrated also that no "burning" of foliage takes place with calcium cyanide, even when concentrations are used much in excess of the corresponding standard dosage of liquid hydrocyanic acid. It has been repeatedly noted that leaves may be thickly coated with the powder itself without any burning being observed.

Since the margin of safety is so much wider when using calcium cyanide, it follows that the number of hours out of the twenty-four which may be used for fumigation may be greatly extended by the use of "powdered hydrocyanic acid." This assumption has been amply borne out by numerous field experiments with daylight fumigation as well as in wet and foggy atmospheres.

The wider range of toxicity of the new product over liquid hydrocyanic acid has the further advantage that it makes possible the eradication of the so-called "resistant scales" which occur in many sections of California. These resistant scales so far have not only survived the highest standard dosage of liquid hydrocyanic acid, but even excess treatment up to defoliation of the tree has failed to secure satisfactory control.

It has been repeatedly demonstrated in field work with "powdered hydrocyanic acid" that there is a difference in the manner in which the scale are killed by the new product. Scale killed by liquid hydrocyanic acid present at first no change apparent to the eye, but after several weeks gradually dry up. On the other hand, when the new product has been used, a decided change in appearance is evident within 6 days and the dead insects have been found to be swelled up or bloated, a condition which has not been observed when killing with liquid hydrocyanic acid.

"Powdered hydrocyanic acid" lends itself to all sorts of fumigation, such as warehouses, ships, mills, railroad cars, etc. Where it is not objectionable to blow the dust into the space to be fumigated, suitable dust guns may be used. On the other hand, the dust may be spread along the floor, through the aisles, or similarly in very thin layers and in predetermined amounts by suitable appliances, or air may be blown through the dust, held in a suitable filtering receptacle, such as a bag.

No doubt many new applications of the new product will be found. On account of its ready solubility in water and a number of organic solvents, numerous applications of "powdered hydrocyanic acid" suggest themselves.

Acknowledgment

The author wishes to acknowledge the assistance of R. W. Poindexter, Jr., of the California Cyanide Company, and of his associates, C. E. Swift and P. T. Dolley, in carrying the operations from the laboratory to full-scale plant production.

Dewar Flasks in Physical Chemistry Laboratory Exercises

By Aubrey C. Grubb

UNIVERSITY OF SASKATCHEWAN, SASKATOON, CANADA

I N MOST laboratory manuals the procedure for the determination of the heat of neutralization of acids and bases in dilute solution involves considerable chance of error for the average student in physical chemistry. In the first place the calorimeter of the Fritz Kohler type or a "modification of that devised by Thomson" demands most careful manipulation to eliminate errors due to radiation, heat capacity of the apparatus, and lag effects. Secondly, the students are instructed to use two thermometers, previously compared, one in acid and the other in the alkali. Then at a certain instant one solution is poured into the other. Serious errors are usually found in this part of the work and consistent results are difficult to obtain, owing chiefly to the large personal equation.

In 1921 an attempt was made in this laboratory to use the method described by Mathews and Germann² using a Dewar flask for the calorimeter and introducing down the center a glass tube, containing one of the reagents, closed at the bottom by a piece of rubber. The acid and base were left in the Dewar and stirred slowly until a regular slow change in the temperature reading of the Beckman showed the solutions to be near temperature equilibrium. At this point the rubber was punctured and the total heat change determined.

It was found exceedingly difficult to fasten the rubber securely enough over the end of the glass tube so that diffusion did not take place or no acid or alkali came in contact. To avoid this difficulty a thin bulb was blown at the end of the tube. The bulb can be made thin enough to allow temperature equilibrium to take place much quicker than by using the rubber diaphram. The bulb also eliminates any errors due to diffusion of the two solutions. At the proper instant a slight stroke from the projecting end of the glass stirrer will rupture the bulb and allow the acid and base to mix freely. The maximum temperature change is then quickly ascertained. The advantages of the all-glass apparatus, in spite of the variation in specific heat, are pointed out carefully by White.³

The student can use carefully prepared and standardized acid and alkali to determine the heat capacity of the calorimeter. These values are found to be consistent and very low when compared with the all-metal calorimeter. Moreover, only one thermometer is necessary, which eliminates the chance for error where two instruments are used. The low heat conductivity of the glass vessel adds to the accuracy of the reading for the total temperature change of the mixed solutions. Furthermore, this set-up can be made in much shorter time, stirring can be less vigorous, and, lastly, the students gain some knowledge of the rudiments of cutting and working glass. The jackets of old condensers have been found very suitable for use as central tubes, as they are about the correct diameter for the liter Dewar and have quite thin walls.

This method has been used with very satisfactory results since 1921 at the University of Saskatchewan for the determination of various heats of reaction.

³ J. Am. Chem. Soc., 40, 1890 (1918).

¹ Received November 16, 1925.

² J. Phys. Chem., 15, 73 (1911).