PRELIMINARY TESTS ON A NON-COMBUSTION TYPE SILVER IODIDE GENERATOR

By

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INTRODUCTION

Schaefer (1946) discovered that supercooled water droplets in his cold chamber could be converted to ice crystals by the addition of dry ice. The crystals were formed by lowering the temperature in the vicinity of the dry ice to below the spontaneous freezing temperature of water at near -40C.

Vonnegut (1947) subsequently discovered that ice crystals could be formed at temperatures as warm as -4C by providing ice-forming nuclei of silver iodide.

Although considerable effort has been expended since 1948 to find a more effective ice nucleating material, silver iodide remains as the best known and most effective material for preparation of artificial ice nuclei.

Preparation of artificial ice nuclei from silver iodide

Silver iodide nuclei are usually prepared by rapid quenching of the vapors resulting from heating of silver iodide. Various methods of vaporization have been used. Since difficulty is experienced in controlling vaporization of silver iodide in powder form, a common practice has been to put the silver iodide into acetone which then serves as a carrier. In some versions of silver iodide generators the acetone itself has been used as the combustion agent to vaporize the silver iodide. A more common procedure has been to use the acetone as a carrier with the primary heat of combustion being provided by propane. Coke or charcoal generators use the acetone solution as a carrier to impregnate the combustion agent. Electric arcs and electric furnaces for vaporization have been used less frequently. Pyrotechnic devices, similar to highway flares, have also been used for preparation of artificial ice nuclei from silver iodide.

Design considerations for ice nuclei generators

The following are considered to be desired characteristics of an ice nuclei generator:

1. It should produce large numbers of effective ice nuclei, approaching the theoretical maximum for the range of temperature desired.

2. The unit should be operationally highly reliable.

3. The unit should minimize the cost of operation above the base cost of the silver iodide itself.

4. It should be simple to operate since it is frequently necessary to use untrained operating personnel and to have unattended operations.

5. Photo-decay of the ice nuclei should be minimized.

6. Control of particle sizes, particle size distributions, and impurities is desirable.

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Limitations of existing equipment for generation of ice crystals

Large numbers of effective ice nuclei are produced by the vaporization of silver iodide. Fletcher (1959) has indicated that these approach the theoretical maximum values for at least one type of generator. However, many uncertainties exist in the operating characteristics of existing silver iodide generators. Variations in particle sizes exist which can affect the activation temperatures of the crystals. Various impurities are also introduced in the combustion process which greatly complicate the activation characteristics. Photo-deactivation of silver iodide has been found to occur and to vary greatly with the method of combustion used. Control of particle sizes and chemical impurities are difficult in the combustion process; yet these factors are of importance in determining the activation temperature of ice nuclei and their subsequent photo-deactivation.

One of the greatest problems encountered with silver iodide combustion generators has been that of operational reliability. All types of units have given significant, if not serious operating problems in the field. Rates of production of ice nuclei do not approach the theoretical maximum in some cases, and in addition, the problems of combustion of chemicals in large quantity has imposed limitations for airborne equipment.

While the above limitations are not considered insurmountable, it was believed that additional and improved techniques for generation of ice nuclei should be explored. This paper reports some preliminary tests on a non-combustion approach to the preparation of effective ice nuclei from silver iodide. Even if this approach proves unsatisfactory for general field use the possibilities for controlling impurities, and to at least partially particle size, can make such a unit valuable for further studies of the characteristics of ice nuclei produced from silver iodide.

THE CSU EVAPORATION RESIDUE SILVER IODIDE GENERATOR

Principal of operation

The practicability of using ice nuclei formed by the silver iodide residue left after the evaporation of small carrier droplets is being explored as the basis of a usable silver iodide generator. Silver iodide is placed in a container into which liquid anhydrous ammonia (approx. 2 gm AgI/gm NH_3). The solution is stored under medium pressure at ambient temperatures in the liquid state. The NH_3 - AGI liquid complex is allowed to expand through a nozzle to ambient pressure which results in rapid evaporation of the ammonia (it can exist only as a gas at ambient pressure and temperature except for very low temperatures - about -30C). This rapid evaporation process releases silver iodide crystals.

Subsequent to initiation of work at Colorado State University on the silver iodide-ammonia generator, it was learned that Tominago and Kinumaki (1954) had experimented with a similar generator in Japan.

Description of equipment

The equipment for the generator consists of a standard 25 lb. propane bottle piped as shown in Figure 1. The center connection consists of a valve attached to a standpipe which extends to within 1 inch of the bottom of the bottle. Standard stainless steel tubing is fitted to the valve and runs to a nozzle which is designed to produce a fine spray of ammonia and silver iodide in solution. The second connection is a simple tap on the top of the tank which is connected to the liquid line. This is used for purging purposes. The wet ammonia vapor will dissolve any deposit of AgI in the lines or nozzle. A third connection should be provided for introducing the AgI to the bottle before charging with anhydrous ammonia.

A word of caution is in order. The silver iodide-ammonia complex tends to leak very easily. Thus all connections must be of good quality and workmanship. If threaded joints are used, the thread should be sealed with teflon tape. If flare joints are used, extreme care must be exercised in flaring the joints. Since anhydrous ammonia attacks copper at a rapid rate, any copper alloys should be avoided.

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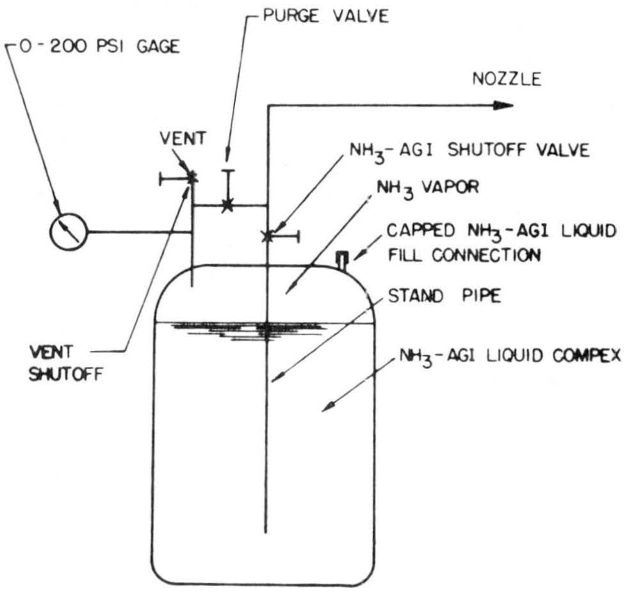

Figure 1.

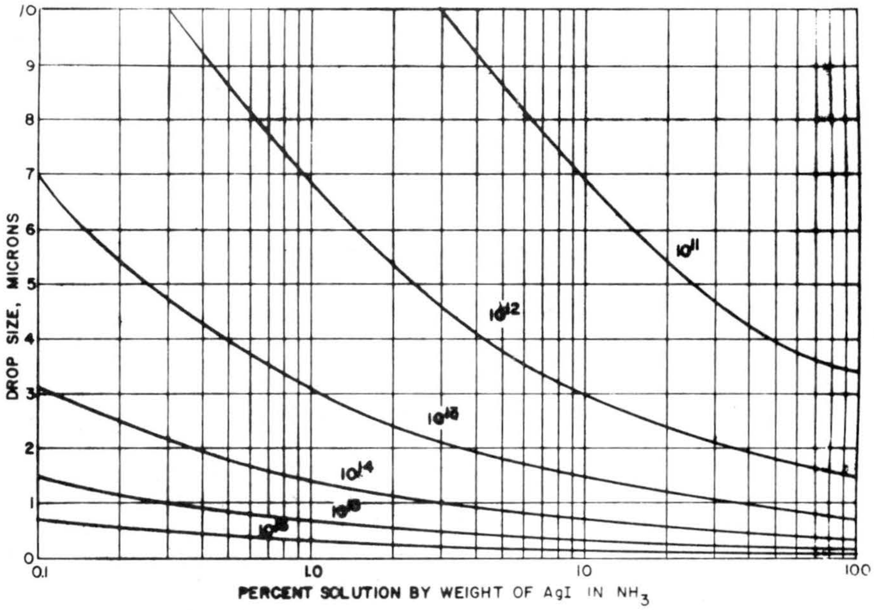

Figure 2.

CALIBRATION TESTS OF CSU EVAPORATION - RESIDUE

SILVER IODIDE GENERATOR

Equipment and procedure for laboratory tests

A technique similar to that described by Vonnegut (1957) and Guquay (1960) is used for calibration of the generator. A steady flow of the ammonia-silver iodide solution is established in the outlet of a wind tunnel. Samples of known volume are withdrawn at the discharge end of the wind tunnel test section and introduced into a cold chamber maintained at -20C for all tests carried out to date (tests at other temperatures are planned). Each effective nucleus is assumed to grow in the supercooled cloud which forms by breathing into the cold chamber. After growth, the crystals fall to the bottom of the chamber where they are collected on a microscope slide and viewed under a low-power microscope. The number of effective crystals is obtained from an average of 5 to 10 individual observations. Individual observations usually do not vary more than by a factor of two or three, and only rarely do individual observations vary by a factor of ten.

For the equipment used, the generator efficiency was determined from the following relation:

$$N = \frac{C}{M S} \times 1.2 \times 10^{12} \qquad (1)$$

where

N = generator efficiency, number of effective ice nuclei per gm. of silver iodide
C = average number of ice crystals observed in the microscope field of view
M = average mass rate of flow of ammonia-silver iodide from the generator nozzle, gms. per min.
S - concentration of silver iodide in ammonia, gm. silver iodide per gm. of ammonia.

Other tests have been conducted which are designed to reduce errors which might result from the short time for vaporization of ammonia in the wind tunnel. A measured quantity of ammonia-silver iodide solution was released in a large closed building having a volume of approximately 750,000 ft^3. Samples were withdrawn from this closed building over an extended time period, and released into the cold chamber, and counted in the same manner as was done for the wind tunnel tests. For this test the efficiency of the generator was computed from the relation

$$N = \frac{C}{M S} \times 3.26 \times 10^{14} \qquad (2)$$

where m - gms. of ammonia-silver iodide released, and the other symbols have the same definition as for equation 1.

Analysis of concentrations and droplet sizes required for suitable generator efficiency

A computation has been made to determine the droplet diameter required for various generator efficiencies (nuclei per gram of silver iodide) based on the assumption of a uniform droplet size. The results are shown n Figure 2. Figure 2 shows, for example, that droplet diameters less than one micron are required for production of 10^{15} particles for all concentrations greater than about 0.3 percent. In order to attain acceptable efficiency of 10^{15} nuclei per gram with a 10 percent solution of silver iodide, it would be necessary to attain a uniform droplet size of about 0.3 micron, but if 100 crystals per droplet could be attained, a uniform droplet diameter of about 1.5 microns would be satisfactory. Dilution of the silver iodide to lower concentrations would also permit larger droplet diameters, but such dilution would improse difficult logistics problems for using such a generator in a light aircraft. (For example, dispersing 500 gram of 0.5 percent solution of silver iodide per hour would require approximately 42 gallons of ammonia per hour, while the 10 percent solution would require only about 2 gallons per hour.)

Laboratory observations of the production efficiency of ice crystals

Results of the tests of generator efficiency which utilized the wind tunnel are shown in Table 1. Test 1 in Table 1 shows typical results of the first tests.

These results, showing efficiency about 10^{12} per gm. repeated over several trials, were disappointing because other generators have been reported to produce crystals in excess of 10^{15} per gram of silver iodide, Fuquay (1960).

Table 1. Results of preliminary laboratory tests of ice crystal output of CSU silver iodide generator.

Test Number	Nozzle Pressure psi	M gm/min	S concentration	C crystal count	N nuclei per gm AgI at -20°C	Remarks
1	128	27.2	0.036	1.7	2.1×10^{12}	
	132	"	"	2.6	3.1×10^{12}	
	138	"	"	3.7	4.4×10^{12}	
	138	"	"	2.8	3.4×10^{12}	
	138	"	"	1.9	2.5×10^{12}	
2	100	33	.0376	1.0	1.0×10^{12}	Distance of sampling point from nozzle 15 ft.
	"	"	"	0.9	0.9×10^{12}	15 ft.
	"	"	"	2.6	2.6×10^{12}	30 ft.
3	98	29.8	0.02	2.5	4.8×10^{12}	Mixing chamber
	100	"	"	2.3	4.4×10^{12}	"
	100	"	"	2.0	3.9×10^{12}	"
	102	"	"	2.9	5.6×10^{12}	"
	100	"	"	2.1	4.0×10^{12}	"
	100	"	"	1.8	3.5×10^{12}	"
4	100	165.7	.0217	17.3	5.6×10^{12}	Air-Atomized Nozzle
	"	"	"	12.7	4.1×10^{12}	" "
	"	"	"	18.5	6.0×10^{12}	" "
	"	"	"	18.2	5.9×10^{12}	" "

Results of tests made by releasing ammonia-silver iodide into a large closed building are shown in Table 2.

Table 2. Results of preliminary laboratory tests using a large closed chamber.

$m = 1238$ gm
Nozzle: 0.6
$S = 0.02026$

Test Number	Date	Time	N-crystals per gm
5	8 February	2045	15.0×10^{12}
		2143	5.7×10^{12}
		2252	3.7×10^{12}
6	9 February	0845	0.2×10^{12}
		1015	0.2×10^{12}
		Average	5.0×10^{12}

Several variations were made to attempt to increase the efficiency of the generator. The variations and their effects were as follows:

1. The sampling location was located at 15 and 30 feet from the spray nozzle in order to detect any differences that might be caused by the time required for breaking of the spray. As shown in Table 1, test 2, the efficiency was slightly higher for the sample taken at 30 feet than at 15 feet.

2. A mixing chamber (55-gallon drum) was inserted into the outlet of the wind tunnel. Spray from the generator nozzle was released into the drum to give a larger time for the spray to vaporize prior to taking the sample for testing. As shown in Table 1, test 3, the efficiency did not charge appreciably.

3. An air-atomized nozzle was used to attempt to get a better atomization of the ammonia. As shown in Table 1, test 4, results were about the same as for the previous tests.

Results of preliminary field tests

A portable version of the CSU generator was taken to the 1963 Yellowstone Research Seminar in January 1963. (The seminar was conducted by the Atmospheric Science Research Center, State University of New York). The generator was used to seed supercooled clouds in the Old Faithful Geyser Basin on 12 and 14 January 1963. On both days, optical effects (22° Halo and Parhelia) were noted shortly after beginning of seeding. A portable cloud particle replicator* was operated on both days. The following is quoted from a report by Todd and Hindman (1963):

> "Long sequences of replicas were taken once on the morning of January 12 which started when the temperature was below -40C. During this time the geysers' clouds were spontaneously nucleating and the replications were of frozen droplets. As the temperature warmed up to -37C Schleusener operated his Ammonia AgI generator during which time there were numerous columns...
> After seeding stopped ice fell out and no more diamond dust appeared in the air and replication showed only water droplets at temperature of -34C.
> On January 14 there was another opportunity to observe the effects of seeding from Schleusener's generator. On this occasion the generator was operated in the Old Faithful area and samples were taken from Old Faithful west down the Firehole River almost to the Castle Geyser area and a vast number of clear replicas were obtained. After the ice crystals settled out from the seeding the replicator was used to catch water precipitation from the cloud that forms over Blue Star pool."

Figure 3 shows replicas of cloud particles obtained from the MRI cloud droplet sampler after seeding with the ammonia generator.

Additional evidence that the generator was effective in producing ice nuclei was obtained by Dr. J. P. Lodge, who examined ice crystals from a seeded plume and found that all of the crystals revealed recoverable nuclei after being warmed to a temperature warmer than ± 0C. This test indicates that the nuclei were artificial. (Lodge, 1963).

COMPARISON OF CRYSTAL COUNTS WITH DROPLET SIZE DISTRIBUTIONS

Replicas were made (using the formvar technique) of the effluent from the ammonia silver iodide generator. Figure 4 shows the drop-size distributions observed.

The droplet size distribution as a function of distance from the nozzle is shown

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* Under development by Meteorology Research Inc., Altadena, California.

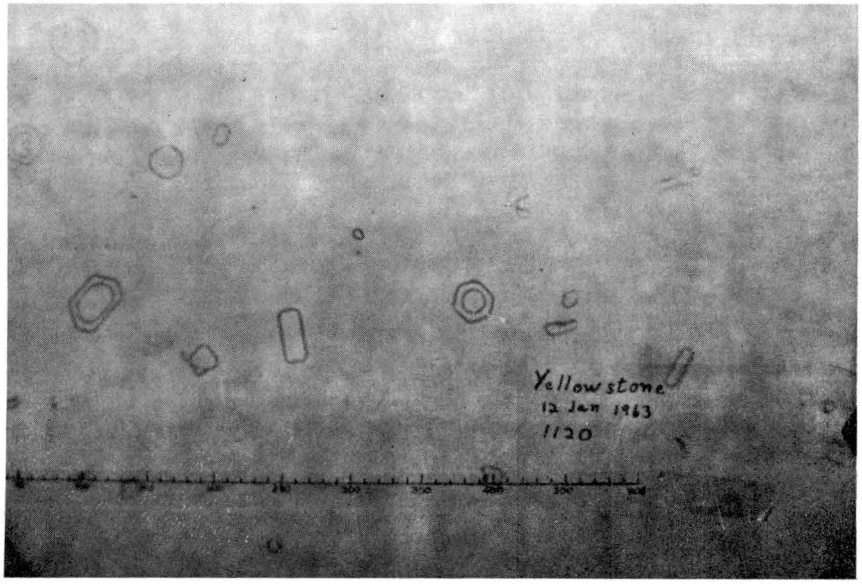

Figure 3.

Replicas of ice crystals obtained from a cloud seeded with ammonia generator. Yellowstone Old Faithful Geyser area, 12 January 1963. (Photo courtesy of Meteorology Research, Inc.)

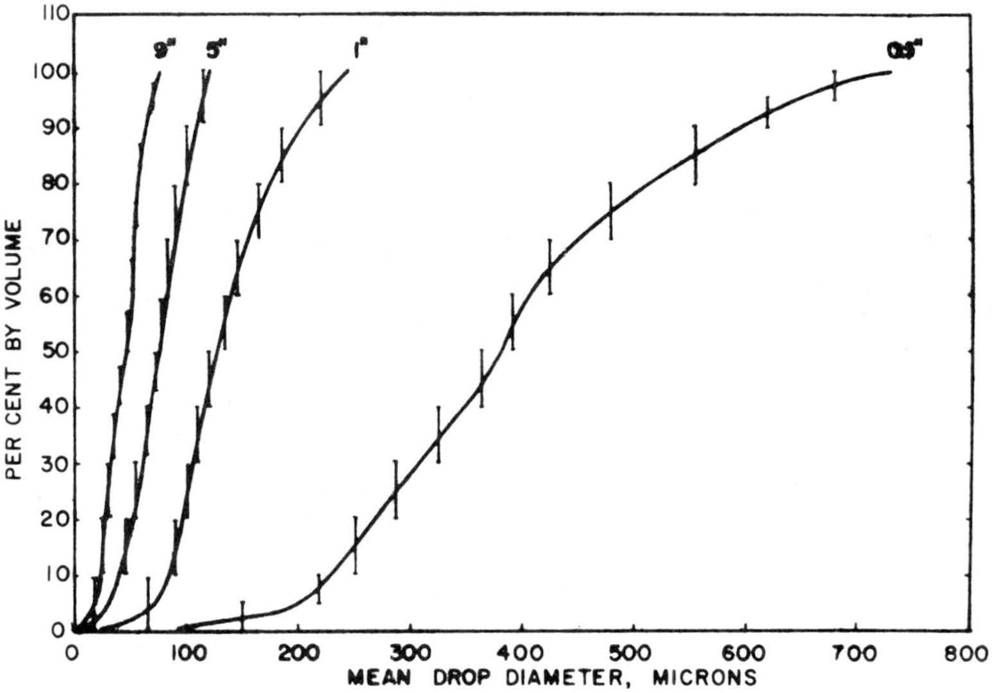

Figure 4.

in Figure 5 for the median, 90 percent, and 10 percent droplet diameters.

Using the drop-size distribution of Figure 4, the number of droplets per gram of silver iodide was computed as a function of distance from the nozzle, making the assumption of constant concentration of 2.07 percent of silver iodide by weight, and the assumption that the diameter of the imprint on the formvar was 1.5 times the diameter of the droplet. The latter assumption is based on the work of MacCready (1962) on the replication of water droplets. The results of this computation are shown in Figure 6.

Comparison of Figure 6 with the results of Table 2 indicates approximately two orders of magnitude difference between crystal counts (5×10^{12}) and computed droplet numbers (10^{10}). This difference between the computed number of droplets and the observed number of crystals suggests that individual ammonia droplets break up in such a fashion as to permit the formation of more than one effective ice nucleus per droplet -- perhaps as many as 100 per droplet. This conclusion must be considered tentative, because of uncertainties in the sampling technique, particularly for the very small droplets.

However, a further computation tends to support the hypothesis of more than one crystal per droplet. Consider the median diameter at 0.5 inch from the nozzle (Figure 4). Assuming a 3 percent concentration by weight, the volume of the silver iodide in a droplet 380 microns in diameter would be equivalent to a sphere of approximately 56 microns diameter. It will be noted from Figure 5 that the median droplet size is less than 56 microns at about 7 inches from the nozzle. Hence, it is inferred that there must have been a loss of silver iodide as ammonia evaporated from the droplet between 0.5 and 7 inches from the nozzle. A similar computation for the 90 and 10 percent droplet diameters yields similar results. This last computation was based on a ratio of $\left(\frac{\text{imprint diameter}}{\text{droplet diameter}}\right) = 1.0$. A similar computation for ratios 1.5 and 2.0 indicates pure silver iodide drops at distances of approximately 10 and 14 inches from the nozzle, which lends further support to the hypothesis that the breakup of ammonia droplets leads to the production of more than one silver iodide crystal per drop.

It should be emphasized that the foregoing onclusions are tentative, and subject to further experimental verification. The significance of this phenomena, if real, may be inferred from Figure 2, which indicates that efficiency of 10^{15} per gm. should be possible with uniform droplet diameters of about 1.5 microns, using a 10 percent solution of silver iodide in ammonia, assuming 100 crystals per droplet.

SUMMARY AND PLANS

The preliminary tests conducted to date indicate that the ammonia generator is capable of producing effective ice nuclei. The nuclei have sufficient stability to retain their effectiveness for a period in excess of six hours when retained within a closed chamber. The decay rate when exposed to ultra violet light has not been established. The efficiency (approximately 5×10^{12} nuclei per gram of silver iodide, effective at -20C) is not satisfactory for field use, but the other advantages of using this type of nuclei generation is sufficient to warrant further investigation with the objective of improving the efficiency.

Comparison of crystal counts with observed droplet size distributions suggests that more than one ice crystal is being produced from each droplet of ammonia.

Further work on the generator is planned to attempt to develop a generator of acceptable efficiency and satisfactory operating characteristics.

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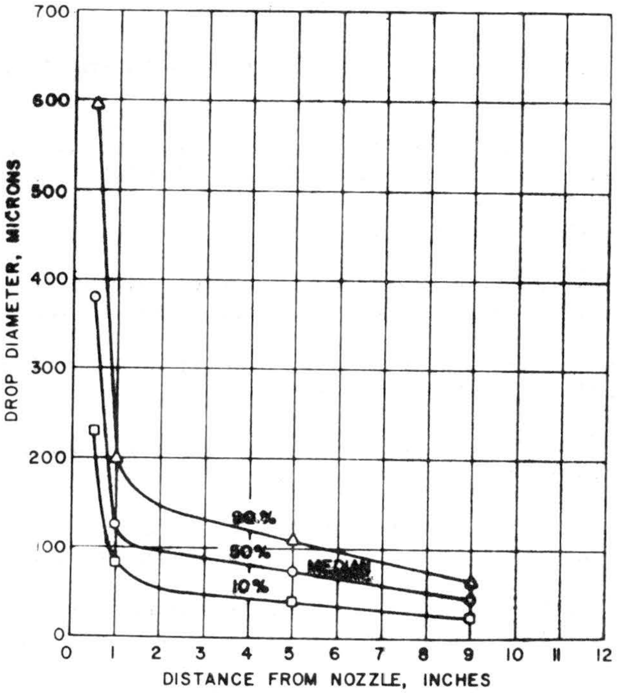

Figure 5.

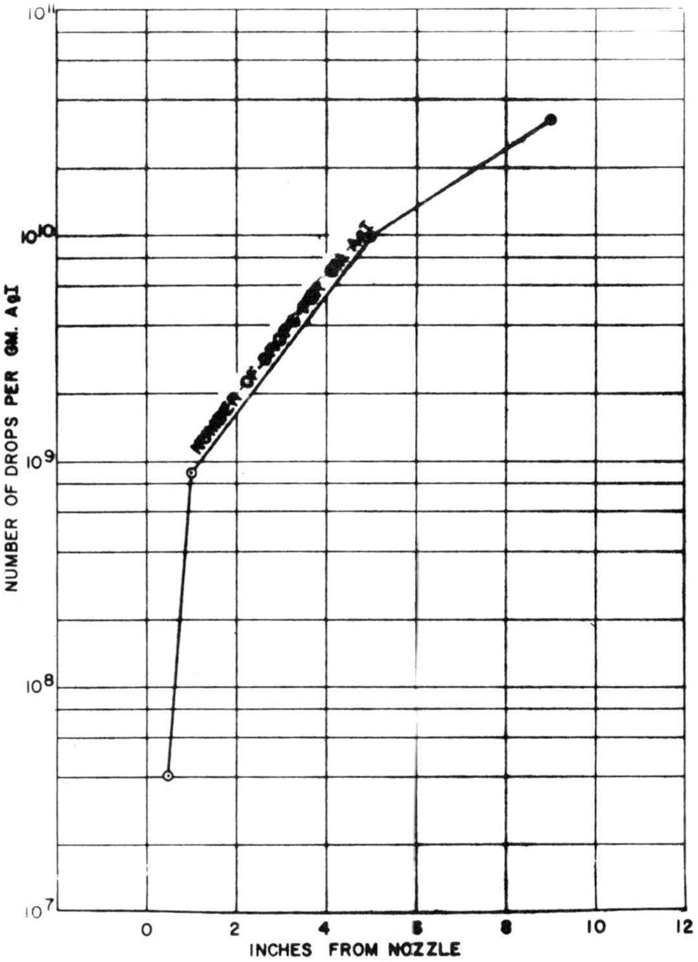

Figure 6.

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