

## SOME CHARACTERISTICS OF A SIEMENS OZONIZER.

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For a number of years the Engineering Experiment Station at Purdue University has been conducting an investigation entitled, "The Fixation of Atmospheric Nitrogen by the Silent Discharge Process." In the course of this work a study has been made of certain types of discharge tubes, and very brief discussion will be given here of some of the results of the tests on the Siemens tube.

## Discharge Tube and Absorption Apparatus.

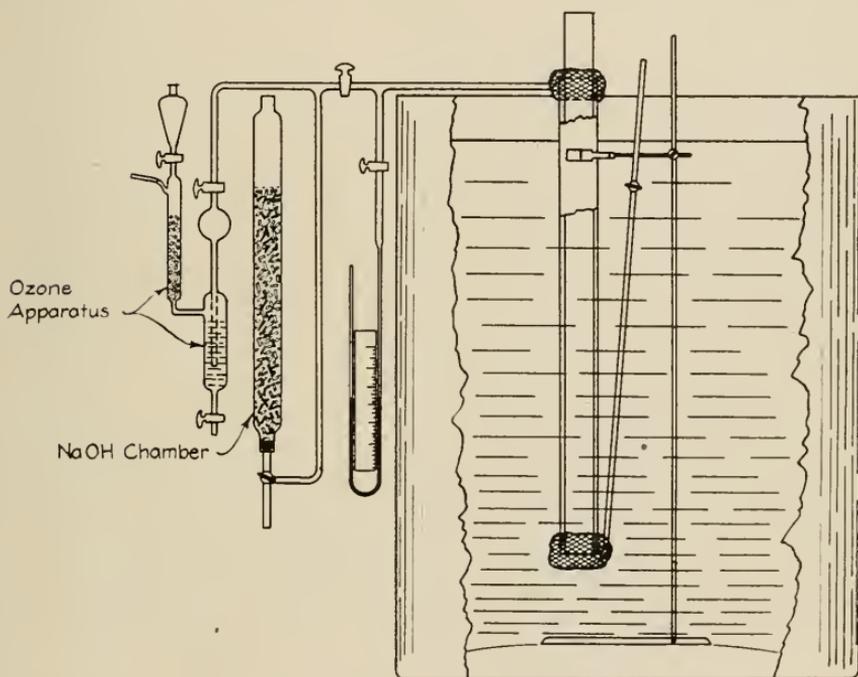


Fig 1.

An idea of the construction of this tube may be gained by reference to Fig. 1, which shows the tube supported by a ring stand in a tank of cooling water. The tube was constructed of two glass tubes arranged concentrically, the inside one being sealed at the bottom. The space between the two tubes was closed at either end with paraffine, and small tubes so placed that air could enter at one end of the annular space and leave at the other end. The radial length

of the annular discharge space was approximately 3 mm., the outside diameter of the inner glass tube being 33.5 mm., and the length of the discharge space, 50 cm. The volume of the discharge space was found by actual measurement to be 166 cc. The inside tube was filled with acidulated water, and this together with a spiral of No. 18 copper wire placed inside the tube acted as the high tension electrode. The water surrounding the tube, which was made conducting by the use of NaCl, was grounded through the medium of the metal containing tank connected to the ground. A spiral of wire was wound around the outside of the discharge tube and connected to ground to insure even distribution of voltage over the entire length of the tube.

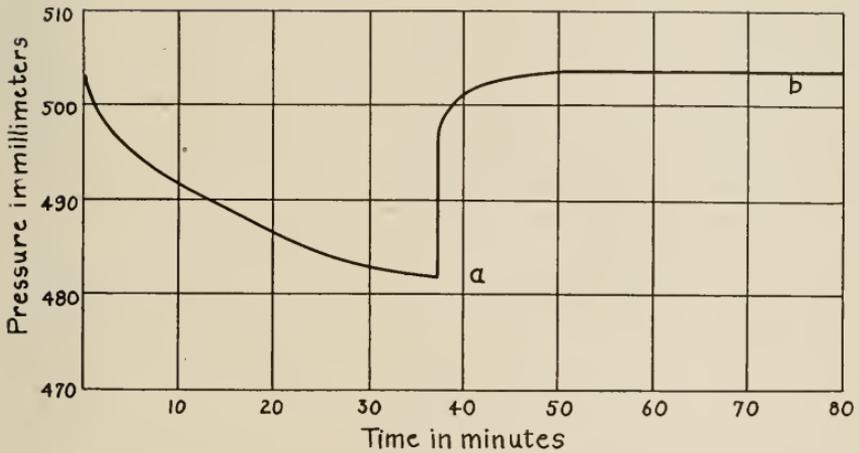
Absorption apparatus consisting of broken glass tubing placed inside a tower was connected as shown in Fig. 1. Sodium hydroxide was used in most cases as the absorbing liquid. In some cases the gases were passed through a KI solution from which the ozone yield could be determined by titration with sodium thiosulphate. The inlet and outlet tubes were provided with stop cocks so that the tube could be completely closed and the pressure of the gas in the discharge tube measured by the mercury manometer. Alcohol thermometers were placed in the liquid inside the inner tube of the discharge tube and in the cooling water surrounding the tube. Means were provided whereby dry air could be passed through the discharge space, the air having been dried by the use of sulphuric acid, after which it passed through a chamber containing soda lime.

Two sources of power were provided for producing the required electric potential to break down the air in the space between the two tubes, one of these being a large induction coil and the other a high voltage transformer. The induction coil was operated from a 110-volt direct current source and was provided with a rheostat in series for varying the high tension voltage. This coil is capable of delivering a spark between needles of more than 30 cm. in length. The high tension transformer, rated at 50 kva. 200,000 volts, was connected to an alternator giving practically a sine wave. This transformer has been arranged so that the current in the secondary winding may be read directly. The high tension voltage was determined by calibrating the tertiary coil, with which the transformer was provided, against the sphere gap standard of the A. I. E. E.

#### TESTS ON ENCLOSED VOLUMES OF DRY AIR.

All of the tests which will be reported in this paper were made upon enclosed volumes of dry air, using either the induction coil or the high tension transformer. Only tests which are more or less typical will be given here, and represent but a small part of the total number of tests made. Correction for pressure change due to increase of temperature as the run progressed was not made, although in many cases the temperature rise curve is shown, this temperature being invariably that of the inner electrode. The temperature of the outside of the tube did not change materially on account of the large body of cooling water which was agitated frequently.

## Exp. No.3.



a - 5.6 vol. % NO

FIG. 2.

b - 6 vol. % NO

The curve in Fig. 2, taken from Spiel,\* who made tests on a Siemens tube with induction coil supply, shows a decrease in pressure with time, until a reversal point is reached, after which the pressure rises rapidly, coming back to nearly if not quite the original pressure.

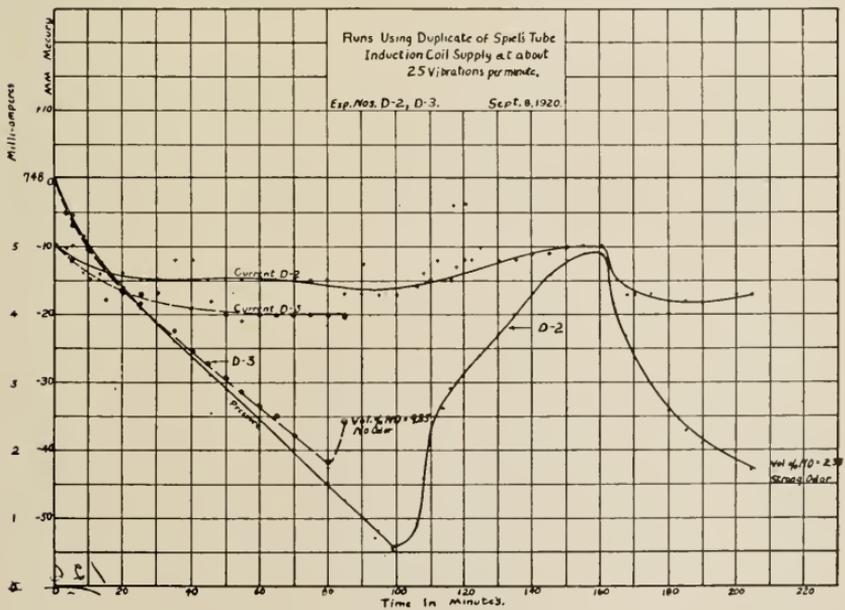


Fig.-3.

\* The Formation of Nitric Oxides by the Silent Electric Discharge in a Siemens' Tube, by Hugo Spiel, Doctor's Thesis, The Technical High School; Vienna, 1909.

At the reversal point a concentration of 5.6 per cent calculated as NO was obtained, while at the point b after the pressure had become constant concentration of only 0.6 per cent NO was found. Spiel concludes that no lower oxides of nitrogen are formed, only  $N_2O_5$ . Spiel determined the concentration at the reversal point by making a second run holding all the conditions as near like the first run as possible. It has been found, however, by plotting the data which Spiel gives, that the pressure time characteristic was not the same for both runs, and this condition is one which the author of this paper has found to exist in all the work done at Purdue with enclosed volumes of air.

Characteristics, different from anything reported by Spiel, appeared when the first run was made on the discharge tube, after being set up, using the induction coil for power supply. The changes in current and pressure with time may be seen by reference to Fig. 3. The current shown is the actual current and was measured in the ground connection of the cooling tank. The full line curve marked D-2 represents the first run, which was continued for 205 minutes. The pressure seemed to go through a cyclic change which also appeared in the current to some extent. A second run (D-3) was made, giving quite different current with a reversal at a higher pressure coming 20 min-

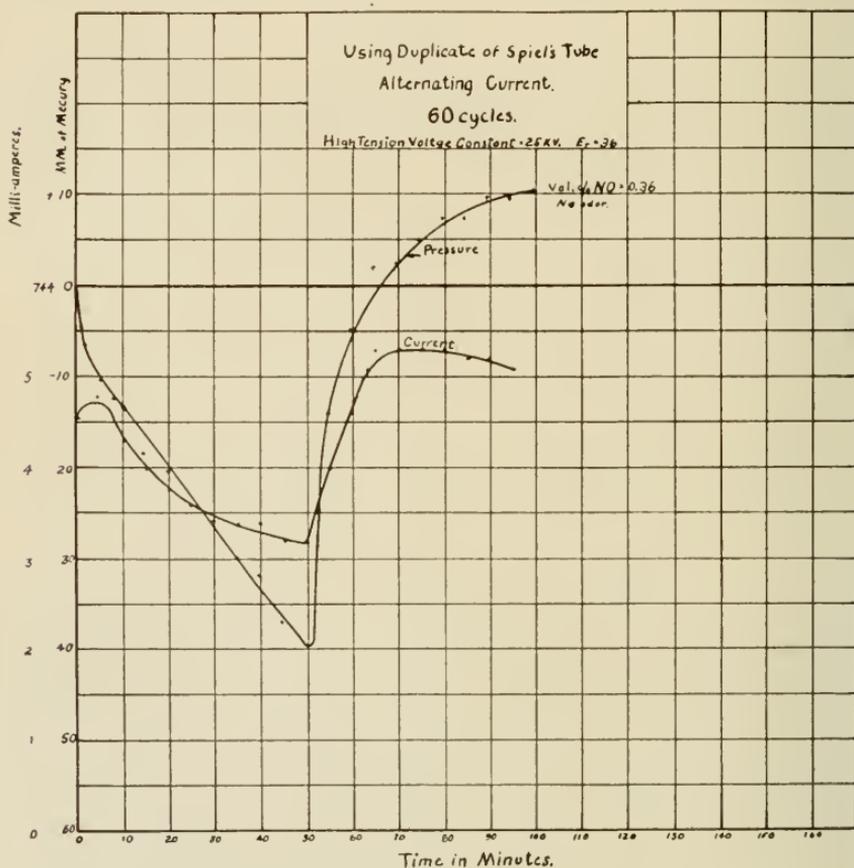


Fig. 4.

utes sooner than in the first run. The concentration of NO at the end of the first run, at a pressure of  $-42.5$  mm. was 2.3 compared with a concentration of 9.35 per cent NO at  $-42.0$  mm. Here the pressures are practically the same and yet the products are quite different. Several runs were made later in the attempt to check the cyclic change in this run, but without success.

Another run under the same conditions was made and stopped at the reversal point, which occurred at 130 minutes with an NO concentration of 9.9 per cent, the tube current being 3 milliamperes compared with 4 and 4.5 milliamperes for the first two runs. Although 34 runs were made, following these first two runs, yet in every case the concentrations were much lower than in these first two runs.

Using the transformer supply, the curves shown in Fig. 4 were taken, the high tension voltage being held constant. The same reversal occurred here as before, but the pressure increased very rapidly after reversing and at the end of the run a concentration of 0.363 per cent NO was obtained. The second test with alternating current (D-8), reversed at a pressure about 7 mm. higher than did D-7, but the reversal in both came at 50 minutes. The concentration at reversal with alternating current was 2.48 per cent NO, which is considerably less than was obtained with the induction coil. The variation of the tube current should be noted since the current curve follows the pressure curve more or less in shape. Another run with the transformer was made at 31 cycles, which was as near the 25 vibrations per second of the induction coil as could be obtained. The pressure in this run reversed at 53 mm. below the initial pressure of 740 mm. after an exposure to the discharge for 110 minutes. The concentration at this point was 3.21 per cent NO.

From these results it is clear that the yield of nitric oxides, which may be discovered by the titration of NaOH for the determination of acid formed, is not proportional to the pressure decrease as might be expected. To get some idea of the concentration for different times of exposure to the discharge with both the induction coil and the alternating current, a series of runs were made which are tabulated in Table I.

TABLE I.

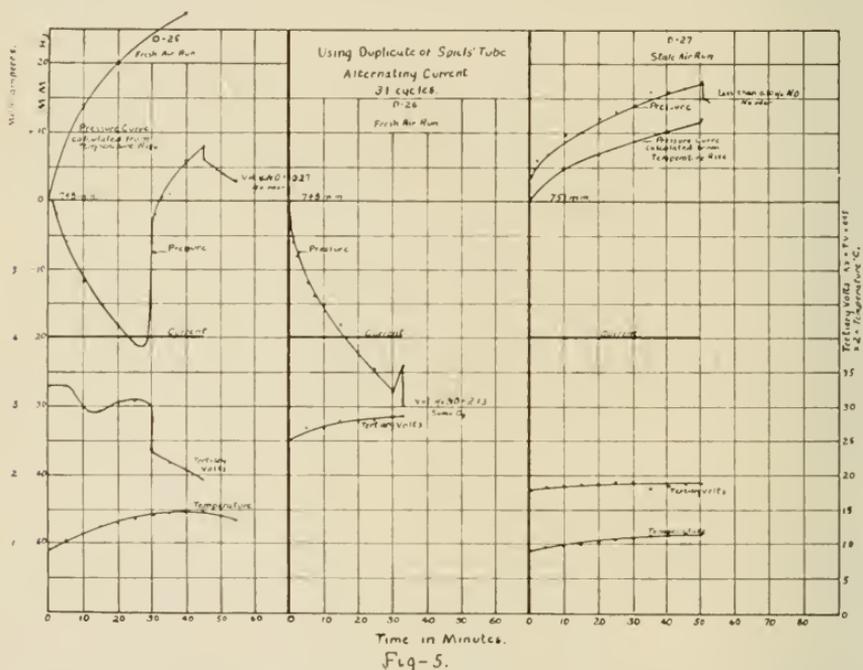
No. D—	Length of Run (min.)	Pressure Decrease at end of run (mm.)	Percent NO. at end of run	Concentration	
				per mm.	per min.
Induction coil runs—Frequency—25					
13	10	-12.5	0.073	0.0058	0.0073
14	20	-16.5	1.00	0.062	0.05
14.5	40	-25.5	1.88	0.074	0.047
15	60	-34.0	2.12	0.082	0.035
Alternating Current Runs—Frequency—31					
10	10	-12.0	1.52	0.127	0.152
11	20	-17.5	1.91	0.109	0.09
12	40	-26.0	2.11	0.081	0.07

Although the average current for the alternating current runs listed in Table I was less than for the induction coil runs, yet the

concentration per millimeter, and per minute, are higher, indicating that under the conditions examined, the use of alternating current increases the speed with which the nitric oxides are formed. It should also be noticed that the concentration per millimeter pressure change increases with the length of run using the induction coil, but decreases with alternating current, indicating that short alternating current runs are advantageous.

Several runs were made to discover, if possible, the reason for the lack of consistent results, but the results were erratic, the pressure reversal varying both as to time and pressure decrease. The yields of nitric acid were different with each run and seemed to vary erratically also.

The usual practice before beginning a run was to sweep out the tube with dry fresh air. On one occasion this sweeping out process was omitted and the results were quite surprising. The tube had stood over night, the products of the last run having been blown out the night before. Instead of decreasing, the pressure increased 17 mm. in 50 minutes, the titration at the end of the run showing only a trace of nitric oxides and no odor of ozone could be detected. Two



other runs, D-25 and D-26, were made under all the same conditions, except that the tube was swept out with fresh dry air just before applying the voltage. The curves showing the characteristics of these three runs are found in Fig. 5.

The pressure time characteristic with fresh air (run D-25) shows three distinct parts, viz., the pressure decrease; the pressure increase to initial pressure and the pressure rise after reaching the initial pressure. A very small yield of NO was obtained from this run, while

more than eight times the concentration of NO was obtained at the reversal point on run D-26, which was made under the same conditions as D-25.

Several runs were made to determine whether or not the pressure rise could be duplicated, and it was found that it could be reproduced as desired, using either the induction coil or the alternating current. Whether or not the same result would have taken place in a new tube of different construction is not known.

The experiments made on fresh air compared with those made with air which has stood in the tube for a considerable period show a very marked change. When the air is not fresh in the tube, but has stood for some time in the tube following the last application of the high voltage discharge, the pressure rises when voltage is applied, and no appreciable quantity of ozone or nitric oxides are to be found. The corona discharge is more noisy and appears to consist of many sparks and points. This condition is much like that after reversal when fresh air is used, for immediately upon reversing the discharge changes from a quiet blue glow to noisy streamers and condensed discharges, which condition increases as long as the pressure increases. Although the shape of the pressure rise curve differs somewhat when using stale air compared to the rise above the initial pressure when using fresh air, yet, all the evidence obtained goes to suggest that in some manner the air standing in the tube is carried through the equivalent of a reversal and subsequent pressure rise. The air standing in the tube may well be affected by some traces of the products of the previous run, this action being catalytic in its nature. Such traces may remain occluded in the glass or in a very dilute state in some air pocket.

Run No. D-28 was made in an effort to secure more information concerning the way in which the contamination took place. This run followed D-27 with an interval of 23 hours. The air was swept out of the tube following D-27 in the usual manner, allowing about 15 minutes for absorption. The tube was then closed up for 3 hours, after which fresh dry air was blown through at a rapid rate for 3 hours. The tube was again closed up, and the next day, after an interval of 17 hours, run D-28 was made. Reversal took place at 30 minutes after the pressure had decreased 28 mm. Titration at this point gave a concentration of 0.4 per cent NO, while but a trace of ozone was observed.

From this experiment it appears that the effect of contamination is reduced by sweeping out the products after a run, using a large quantity of air. In case the tube stands for a considerable length of time, even though the tube has been carefully swept out, the yield is materially affected as in D-28, where the yield was about one-eighth of what it was in D-29, which was a check run with fresh air. Thus, even small traces of the previous runs serve to greatly reduce the yield. Curves showing the pressure changes for D-28 and D-29 will be found in Fig. 6.

The results from the use of a discharge tube not only vary with the design but also vary greatly with tubes of the same design. A second tube built of pieces of the same tubing and having practically all the same dimensions as the tube described in the first part of this



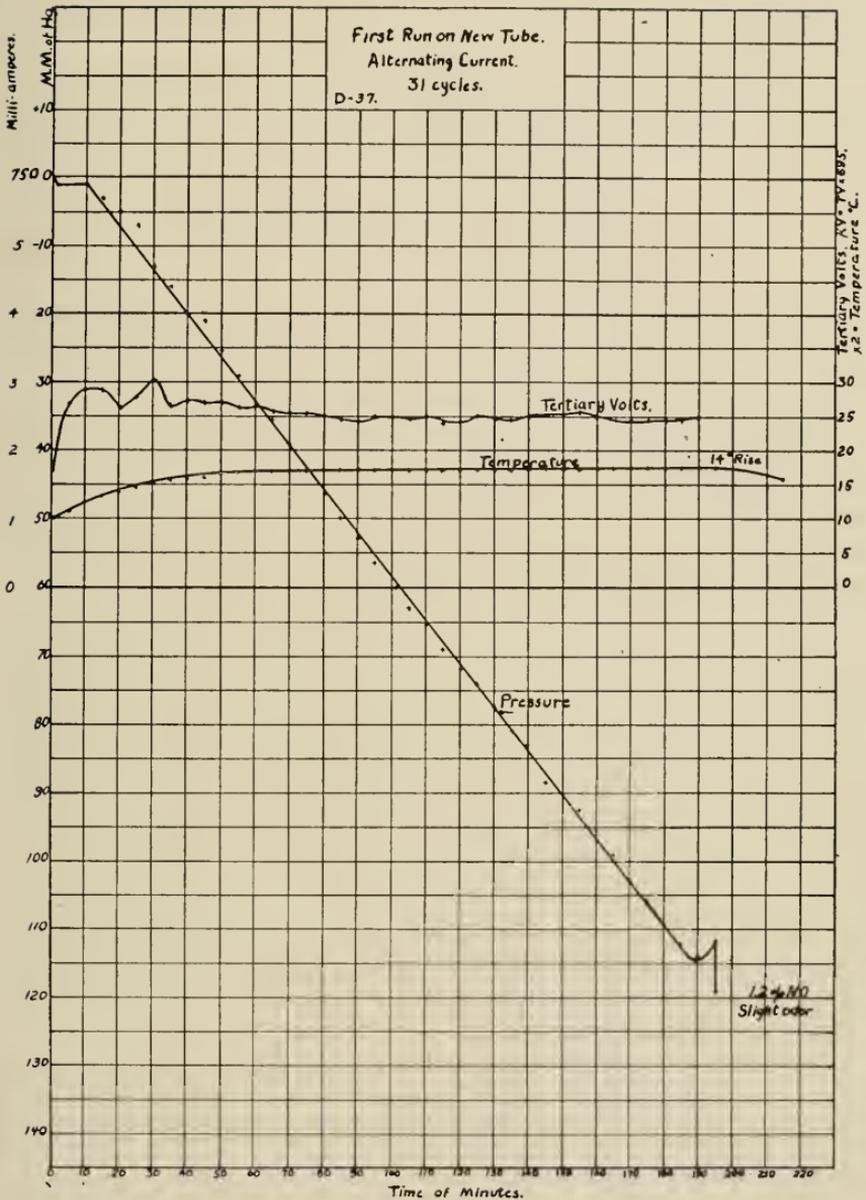


Fig.- 7.

2. When air in the tube has been in contact for a considerable period with other air which has been previously subjected to electrical discharge, the usual pressure decrease is modified, the yields diminished, and in case sufficient contamination has taken place the characteristics of the tube changed altogether, the pressure increasing instead of decreasing and the yield greatly reduced or eliminated altogether.

3. While it is true that the discharge is more or less erratic in a given tube, yet there seems to be some foundation for the statement

that different tubes of the same design and of similar materials will yield different results.

4. The usual pressure characteristic consists of four parts:

1. The pressure decrease.
2. The pressure increase (usually quite rapid) up to atmospheric pressure.
3. The pressure increase (having the shape of a temperature rise curve) above atmosphere.
4. The abrupt pressure decrease when the power supply is disconnected.

Part 4 always occurs; parts 1, 2 and 3 are to be found together when working with fresh air only, while part 3 only will be found when the air has been sufficiently contaminated.

When the pressure is decreasing the discharge is more quiet and, as a rule, the temperature rise less than when the pressure is increasing. The character of the discharge is also quite different after reversal than before, thus indicating a very definite change in the structure of the air. This statement is also borne out by the fact that changes in pressure are accompanied by corresponding changes in current flow when the voltage is held constant.

5. The pressure decrease is not proportional to the nitric oxides absorbed. The pressure decrease is always greater than can be accounted for by the products absorbed, thus indicating the presence of some heavier molecule. It is true that some of the pressure decrease may be due to some of the gas being driven into the glass, but that this would account for the discrepancy observed seems doubtful. Whether this heavy molecule is a combination of O and N or a heavy molecule of O or N it is not possible to state. It is likely, however, that more than one such combination will be found in the effluent gases.

6. Although not conclusive, the data does show that in most cases the pressure decrease with alternating current is more rapid than with the induction coil. The 10, 20, and 30 minute runs indicate that alternating current may also be expected to produce a higher concentration of nitric oxides in a given time, and especially is this true for the shorter periods of discharge.

Complete data showing the results of tests not only on the Siemens tube but tubes of other design, together with much other material of interest relating to the corona discharge, will be found in a bulletin of the Engineering Experiment Station of Purdue University, to be published in the near future.

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