

$\sigma$  = standard deviation (sigma)  
 $A$  = 5.2% thallium nitrate tagged with thallium-204 (aqueous solution)  
 $C_1$  = liquid poured directly on seeds, with mixing after about 10 seconds  
 $C_2$  = liquid poured on walls of bottle and transferred to seeds via wall  
 $D_1$  = normal rolling-type motion of mechanical mixing (Figure 6)  
 $D_2$  = vigorously shaken by hand in flask for 4 minutes  
 $X'_m$  = average activity for N-kernels  
 $X_m$  = average activity for R- + N-kernels  
 $2 \times X_m$  = borderline activity between kernels with high and normal activity  
 R-kernels = higher activity kernels  
 N-kernels = normal activity kernels  
 R-factor = number of R-kernels divided by total number of kernels  
 S-factor = excess mercurial carried by R-kernels divided by total mercurial  
 T-factor =  $(S/R + 1)$  S-factor divided by R-factor plus 1, relative dose on R-kernels  
 $X_i$  = kernel count (activity in a single measurement)  
 $Q$  = micrograms of mercury per square centimeter, average concentration of mercurial on G  
 $g$  = over-all counting efficiency  
 $c$  = millicuries per microgram of mercury, the specific activity of mercurial  
 $K$  = conversion factor, counts per minute per millicurie  
 $t$  = counting time, minutes  
 $(\sigma_X/X)$  = coefficient of variation for kernel count  
 $(\sigma_K/K)$  = error due to statistical fluctuations  
 $b$  = denotes background activity (c.p.m.)  
 $(\sigma_q/Q)$  = spreading error  
 $N$  = number of analyzed kernels  
 $(\sigma_G/G)$  = variation in kernel surface  
 $(\sigma_q/q)$  = geometrical error  
 $F_1$  and  $F_2$  = operators

$A_1$  = normal dosage of disinfectant A  
 $A_2$  = 0.1 of normal dosage of disinfectant A  
 $H$  = necessary time of exposure of treated kernels on film  
 $E_i$  =  $E_2, E_3,$  or  $E_4$

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## FERTILIZER MATERIALS

### Phosphoric Acid of High Concentration

THE PHOSPHORIC ACID sold as phosphatic fertilizer solution contains about 55% phosphorus pentoxide or 75% orthophosphoric acid. The acid, produced either by the wet process or from phosphorus obtained by the electric-furnace method (11), is used for the production of solid and liquid fertilizers. As a part of its objective to develop methods for producing better and lower cost fertilizers, the Tennessee Valley Authority (TVA) has studied the production and properties of furnace acid of higher concentrations than that available to the fertilizer industry.

In 1937 Durgin, Lum, and Malowan (3) published information on the characteristics of strong phosphoric acids and stated that an acid containing 84% phosphorus pentoxide, called tetraphosphoric acid, was being produced commercially. In 1941 Walthall and Stripplin (12) described the pilot-plant development of a method, involving the combustion of phosphorus with dried air, for the production of phosphoric acid of about this concentration.

In recent work by TVA (9), acid containing 76% phosphorus pentoxide, which is equivalent to 105% orthophos-

phoric acid, has advantages over acids both of lower and higher concentrations. Acid containing about 60 to 75 and about 77 to 83% phosphorus pentoxide crystallized at ordinary temperatures, whereas that containing about 75 to 77% phosphorus pentoxide remained liquid at temperatures low enough to be shipped and stored in tanks exposed to the weather. Acid containing about 84% phosphorus pentoxide also remained liquid, but it was much more viscous than the acid containing about 76% phosphorus pentoxide, which has been called "superphosphoric acid," and has been

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A phosphoric acid containing 76% phosphorus pentoxide, "superphosphoric acid," has properties of industrial importance. It contains about 70% more phosphorus pentoxide per unit volume than the acid in common use; it is less corrosive to metals; it is fluid at room temperatures; roughly half of its phosphate is in the ortho form and the remainder is largely in the pyro form; it is more viscous than ordinary furnace acid at room temperature; and it may be diluted with water readily to lower concentrations. Superphosphoric acid has been produced from phosphorus in trial runs of the TVA plant used regularly to produce ordinary furnace acid. The cost of operation was not significantly higher. The plant and its operation are described.

produced satisfactorily in a plant designed for the production of ordinary phosphoric acid. This paper gives properties of acid of 76% phosphorus pentoxide content as well as its advantages and possible uses. The plant used for production of the acid is described, and data on its operation are given.

### Properties of Superphosphoric Acid

**Chemical Composition.** Durgin, Lum, and Malowar. (3) tentatively concluded from analytical and physical studies that strong phosphoric acids consist of equilibrium mixtures of ortho, pyro, and meta acids, with the possibility that other polyphosphoric acids exist at some concentrations. Later, Bell (7) found that orthophosphoric ( $H_3PO_4$ ) and triphosphoric ( $H_3P_3O_{10}$ ) acids were present at concentrations in the range of 72.4 to 88.7% phosphorus pentoxide and that pyrophosphoric acid ( $H_4P_2O_7$ ) was present from 72.4 to 85% phosphorus pentoxide; he found that acid having more than 83% phosphorus pentoxide contained metaphosphoric acid in the form of a polymer  $[(HPO_3)_n]$ . More recently, Huhti and Gartaganis (6), employing paper chromatography, studied the composition of acid in the range of 68.8 to 86.3% phosphorus pentoxide. They reported that acid of 68.80% phosphorus pentoxide content contained phosphoric acid only in the ortho form; pyrophosphoric acid began to appear in an acid containing 69.81% phosphorus pentoxide and increased to a maximum in an acid containing 78.02% phosphorus pentoxide; triphosphoric acid began to appear in an acid containing 74.26% phosphorus pentoxide and tetraphosphoric acid ( $H_6P_4O_{13}$ ) in an acid containing 75.97% phosphorus pentoxide.

The data of Huhti and Gartaganis (6) indicate that superphosphoric acid of 76% phosphorus pentoxide content would contain about 49% of its phosphate as ortho-, 42% as pyro-, 8% as tri-, and 1% as tetraphosphoric acid. The presence of polyphosphoric acids gives the acid an important advantage over ordinary 75% orthophosphoric acid which contains phosphate only in the ortho form.

The acid may be easily diluted by mixing with water. Heat is evolved,

and hydrolysis of the polyphosphoric acids to orthophosphoric acid is rapid.

Data are reported in the literature (4) for heats of dilution of phosphoric acid of an initial concentration as high as 72.4% phosphorus pentoxide (100% orthophosphoric acid), but no such data are available for acids of higher concentrations. Several observations were made of the temperature rise resulting from the dilution of more concentrated acid during the present studies. Acid containing 76% phosphorus pentoxide was diluted to 72.4%, and a temperature rise of about 25° F. was observed. Acid of the same initial concentration was diluted to 55% phosphorus pentoxide (75% orthophosphoric acid), and a temperature rise of about 80° F. was observed. With more dilution the temperature rise was not as great because of the increased amount of dilute acid available to absorb the heat.

**Density.** The densities of phosphoric acids in the range of concentration from that of orthophosphoric acid to that of pyrophosphoric acid have been studied by a number of investigators (3, 4, 7), and the data have been employed (4) in the derivation of the equation

$$d = (0.7102 + 0.01617c) - (11.7 \times 10^{-4} - 6.00 \times 10^{-6}c)t$$

in which  $d$  = density, grams per milliliter;  $c$  = concentration of acid, % phosphorus pentoxide; and  $t$  = temperature, ° C.

This equation was used in the preparation of Figure 1, which shows isotherms of density vs. concentration for acids in the range of 72 to 78% phosphorus pentoxide. The density of acid containing 76% phosphorus pentoxide is 1.92 at 80° F., equivalent to 16 pounds per gallon.

**Viscosity.** The viscosities of acids of several concentrations, including 71.8% and 77.1% phosphorus pentoxide, were determined (3) over a range of temperatures from 85° to 300° F. These data are plotted in Figure 2 as two solid lines, and dotted lines have been drawn as graphical interpolations. Viscosity measurements were made by TVA of three acids of intermediate concentrations at 77° F. The measured viscosities at this temperature were in essential agreement with the interpolated values. The viscosity of acid of 76% phosphorus pentoxide content is 780 centipoises at 80° F. as compared with about 17 centipoises for acid of 55% phosphorus pentoxide content (75% orthophosphoric acid).

Some systems designed for flow or

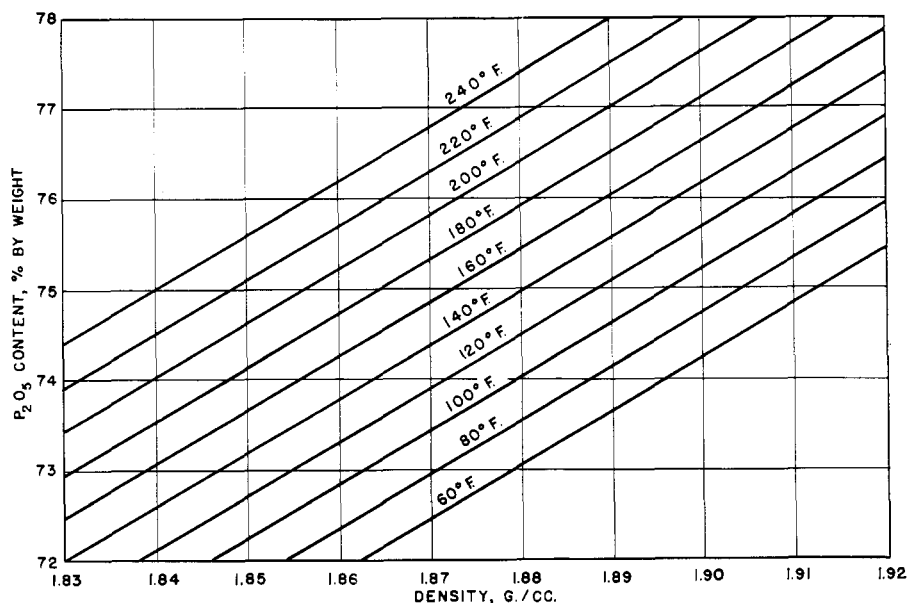


Figure 1. Density of phosphoric acid of 72 to 78% phosphorus pentoxide content

metering of phosphoric acid of the usual concentration (75% orthophosphoric acid) may require modification to adapt them to the use of superphosphoric acid because of its higher viscosity. For example, to permit the use of superphosphoric acid in a system designed for gravity flow of 75% orthophosphoric acid at 85° F. through 15 feet of standard 2-inch pipe, an increase of 0.5 foot of liquid head would be required to deliver an equivalent amount of phosphorus pentoxide as superphosphoric acid. The effect of increased friction losses with the more concentrated acid also could be overcome by increasing the pipe size or the temperature of the acid.

The efficiency of centrifugal pumps would be very low with superphosphoric acid at temperatures below about 100° F. Rotary pumps or gear pumps would be more suitable. Tests showed that, with such pumps, the quantity of phosphorus pentoxide pumped in the form of superphosphoric acid was about 60% of that pumped in the form of 75% orthophosphoric acid against the same head; the power requirement was about 15% greater.

Meters that are essentially independent of viscosity, such as constant-displacement meters or metering pumps, may be used with the acid. In pilot-plant operation, good results were obtained by metering the acid with a metering wheel. This device consisted essentially of a series of cups attached to a wheel that was rotated in a vertical plane in a tank. As the wheel rotated, each cup picked up a constant volume of acid which was spilled into a collecting funnel.

Meters that are sensitive to viscosity changes such as rotameters or orifice meters cannot be used unless the acid is at a fairly constant and elevated temperature. In experiments with a rotameter (Fischer and Porter Flowrator, size 5), good results were obtained in metering the acid at a temperature of 190° ± 5° F. and a rate of about 1 gallon per minute. With larger meters, lower temperatures could be used with equal accuracy.

**Freezing Point.** The freezing point curve for phosphoric acids containing up to 72.4% phosphorus pentoxide (equivalent to 100% orthophosphoric acid) has been determined by Ross and Jones (7). They reported the freezing point of phosphoric acid containing 72.4% phosphorus pentoxide to be 108° F. The freezing point of pyrophosphoric acid which contains 79.8% phosphorus pentoxide was reported by Giran (5) to be 142° F. One of the most important properties of superphosphoric acid, which has a phosphorus pentoxide content between these two acids, is its fluidity at ordinary temperatures. Experience with unrefined superphosphoric acid produced in the TVA plant indicates

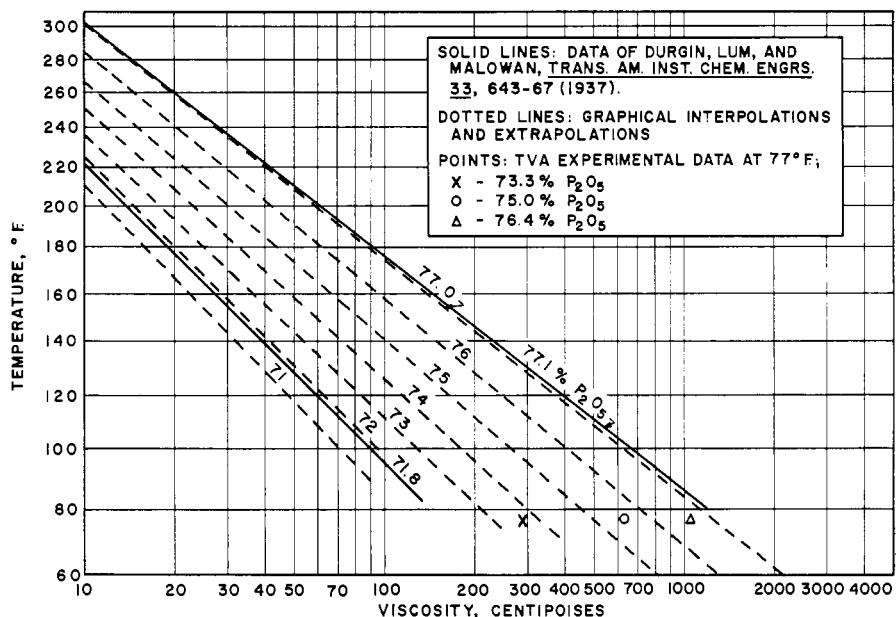


Figure 2. Viscosity of phosphoric acid of 71 to 77.1% phosphorus pentoxide content

that it can be stored in outdoor tanks at 32° F., and even lower, with little likelihood of difficulty from crystallization.

TVA is studying the freezing points of essentially pure acids in the range between ortho- and pyrophosphoric compositions, and the results will be published later. Preliminary results from this study indicate that superphosphoric acid (76% phosphorus pentoxide) approximates a eutectic composition that is approached rather steeply from either side. The shape of the incomplete freezing point curve suggests that the freezing point of the eutectic composition may be above 32° F. for pure acid. Liquids near the eutectic composition have a strong tendency to supercool for prolonged periods, even when seeded—a characteristic that makes exact location of the eutectic quite difficult and at the same time proves advantageous in handling of the acid.

**Vapor Pressure and Boiling Point.** The vapor pressure of the acid at a given temperature is much less than that of ordinary phosphoric acid. The more concentrated acid therefore would be a much better desiccant for drying air or gases. The vapor pressures of phosphoric acid containing up to 63.5% phosphorus pentoxide are given by Farr (4), and those for acids containing from 61.6 to 92.7% phosphorus pentoxide are given by Brown and Whitt (2).

The compositions of the vapors in equilibrium with boiling acids also are reported by Brown and Whitt (2). The data show that the normal boiling point of acid containing 76% phosphorus pentoxide is about 600° F., and that the vapor in equilibrium with the acid at this temperature contains about 1% P<sub>2</sub>O<sub>5</sub> and 99% water.

**Corrosion.** The acid is much less

corrosive to metals and alloys, with the exception of lead, than is ordinary acid. Corrosion data from laboratory tests of these two acids are summarized in Table I. The corrosion rate of mild steel in contact with superphosphoric acid at room temperature was 229 mils per year; this rate was less than half that for ordinary acid but too high to permit the use of mild steel tanks for storing or shipping the acid. A corrosion rate of 60 mils per year is about the maximum acceptable. Studies are being made of corrosion inhibitors that might allow the use of mild steel pipe and tanks with the acid.

Red brass, the common types of stainless steel, and other corrosion-resistant metals showed very satisfactory resistance to the acid at room temperature. Type 316 stainless steel, Hastelloy B, Nionel, and Durimet 20 showed satisfactory resistance at temperatures as high as 240° F. At 220° F., the corrosion rate for Type 316 stainless steel in contact with the acid was only one tenth that with acid of ordinary concentration.

The effects of the acid on several plastic and rubber materials were studied in laboratory tests that lasted from 2.5 to 8 months. The materials tested included those used as bonded tank linings, bag-type liners, and sprayed or painted protective coatings. Buta-Bond (a cured butyl rubber) appeared to offer promise as a bonded synthetic rubber lining for use with the acid. Koroseal, a poly(vinyl chloride) plastic, also appeared to be promising for such use. Painted coatings of Neobon (neoprene-base paint) and of Nukemite No. 40 (solution or vinyl copolymer resins) appeared to be satisfactory.

The preliminary results do not indi-

cate the action of the acid on the plastic and rubber materials given above to be different from that of phosphoric acid of ordinary concentration. The possibility that the more concentrated acid may cause more rapid deterioration of these materials is being studied further.

### Production of Superphosphoric Acid

Superphosphoric acid was produced from phosphorus in the TVA No. 1 acid plant—normally used for ordinary phosphoric acid production in several trial runs. Phosphorus is burned at rates of 2000 to 3000 pounds per hour, depending to some extent on the amount of impurities and water in the phosphorus.

The first superphosphoric acid was produced without modification of the plant, simply by operating it at a higher temperature. Under such conditions, a considerable amount of acid of ordinary concentration, as well as superphosphoric acid, was obtained.

A simple modification was made to the plant which provided for recycling the more dilute acid. This modification made possible the production of superphosphoric acid entirely and provided a means for lowering the operating temperature to avoid increased corrosion of the equipment.

### Description of Modified Acid Plant.

As shown in Figure 3, the plant consists essentially of a vaporizer, combustion chamber, hydrator, and scrubber-separator unit. A more detailed description of the type of equipment used in TVA phosphoric acid plants, including that used for handling and metering phosphorus, has been published (8).

A horizontal steel shell, 8 feet in diameter by 24 feet in length, lined with firebrick is used as the vaporizer. Phosphorus is atomized into the vaporizer, where some of it is burned to supply the heat to vaporize the remainder. The nonvolatile impurities in the phosphorus separate and collect as a slag which is tapped off periodically. The hot gases from the vaporizer pass upward through a vertical duct and into the top of the combustion chamber. Additional air to complete combustion of the phosphorus is supplied at the top of the combustion chamber.

The combustion chamber is built of graphite blocks and has an inside diameter of  $8\frac{1}{3}$  feet and a height of 38 feet. Cooling water flows down the outside of the graphite wall. A portion of the water required for cooling and hydration of the phosphorus pentoxide is supplied through one or more spray nozzles near the bottom of the combustion chamber. The hot gases pass from the bottom of the chamber to the base of the hydrator.

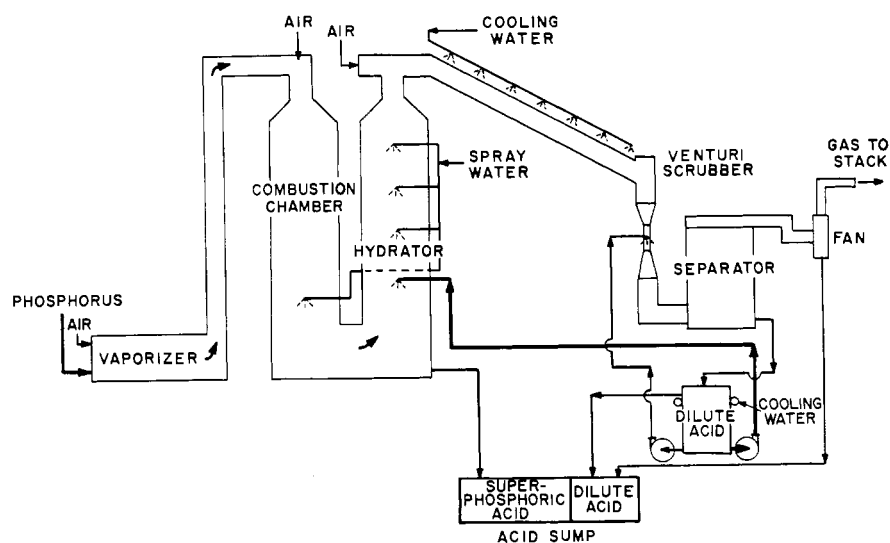
A vertical chamber, about 38 feet high and  $8\frac{1}{3}$  feet wide inside, of octagonal cross section, constructed of carbon blocks, serves as the hydrator.

**Table I. Laboratory Corrosion Tests in Phosphoric Acids without Aeration**

Material Tested	Corrosion Rate <sup>a</sup> , Mils/Year							
	Ordinary Phosphoric Acid, 56.5% P <sub>2</sub> O <sub>5</sub> (78% H <sub>3</sub> PO <sub>4</sub> )				Superphosphoric Acid, 76.7% P <sub>2</sub> O <sub>5</sub> (106% H <sub>3</sub> PO <sub>4</sub> )			
	Temperature, ° F.							
	60-90	120	220	240	60-90	120	220	240
Mild steel	523	..	..	..	229	..	..	..
Red brass	0.4	..	..	..	1.0	..	..	..
Stainless steel								
Type 304	..	..	.. <sup>b</sup>	..	..	..	4.4	..
Type 316	..	..	5.0	..	0.1	..	0.5	1.6
Type 430	..	..	..	..	0.06	..	12.6	..
Nionel	..	..	..	5.2	..	..	..	0.4
Hastelloy B	..	..	..	5.2	..	..	..	0.08
Durimet 20	..	..	..	9.2	..	..	0.1	0.4
Monel	0.1	1.0	..	..	0.08	1.0	..	..
Nickel	0.3	4.2	..	..	0.06	0.9	..	..

<sup>a</sup> A corrosion rate of 60 mils per year is about the maximum acceptance for materials to be used for tanks and pipe.

<sup>b</sup> Excessive rate.



**Figure 3. Flow diagram of plant for superphosphoric acid production**

The remainder of the water required to hydrate and cool the gas is added through four rows of spray nozzles with eight nozzles to the row. The amount of water supplied is controlled by changing the number and size of the nozzles used. In the modification of the plant for the production of superphosphoric acid, dilute acid from the scrubber-separator unit was introduced through the bottom row of spray nozzles. The acid that separates from the gas in the lower part of the combustion chamber and in the hydrator, including that recycled from the scrubber-separator unit, constitutes the superphosphoric acid product. It drains through a water-cooled trough to a sump.

The gases from the top of the hydrator, containing the remaining acid in the form of entrainment and mist, pass through a stainless steel duct to the scrubber. Air for cooling is drawn into the gas stream through an opening in the duct at the top of the hydrator. For the production of superphosphoric acid, provisions were made to water-cool the duct, as shown in Figure 3, to protect it from increased corrosion.

A Venturi scrubber-separator unit of

stainless steel serves to recover the acid mist; recycled phosphoric acid is used as the scrubbing medium. The acid is injected through jets around the circumference of the Venturi throat at a rate of about 55 gallons per minute. The liquid and gas discharged from the scrubber enter the separator. The gas is drawn from the top of the separator by a fan and passed to a stack. A small amount of dilute acid (5% orthophosphoric acid) collects in the fan and drains to the sump. The gas wasted from the stack normally contains less than 0.2% of the phosphorus pentoxide. The acid from the separator drains to a water-cooled tank. Essentially all of the acid recovered in the scrubber-separator unit (5 to 10 gallons per minute) is cooled in this tank and pumped to the hydrator, as mentioned above. The acid recycled to the scrubber also is obtained from this tank. A constant level of acid is maintained in the tank by allowing a small amount of it to overflow to the sump.

**Operating Results.** The results in Table II show how the conditions of operation of the No. 1 plant compared for the production of ordinary acid and

of superphosphoric acid. Results on the production of superphosphoric acid are given both for operation of the modified plant and the plant before modification.

Normally, in operation for the production of acid of the usual concentration, from 40 to 60% of the phosphorus pentoxide input drains from the hydrator as acid with a concentration of about 65% phosphorus pentoxide (90% orthophosphoric acid); essentially all of the remaining phosphorus pentoxide is removed from the scrubber-separator unit as acid with a concentration of about 50% phosphorus pentoxide (70% orthophosphoric acid). The two acids, together with the small amount of dilute acid recovered in the fan, are mixed in the sump and constitute the product. The first column in Table II shows data for a typical period of such an operation.

The second column in Table II gives data for a short period of operation in which superphosphoric acid containing 77.0% phosphorus pentoxide (106.5% orthophosphoric acid) was produced in the hydrator of the plant before modification. The phosphorus rate was increased and the amount of water supplied to the hydrator was decreased to bring about the desired increase in concentration. These changes resulted in higher temperatures throughout the plant. This method of producing superphosphoric acid would result in increased corrosion of the stainless steel equipment and would yield acids of two concentrations. During this period the acid recovery from the scrubber was kept separate from that produced in the hydrator; it contained 40% of the total phosphorus pentoxide and had a concentration of 57.5% phosphorus pentoxide (79.5% orthophosphoric acid).

The plant then was modified to increase the amount of heat removed so that temperatures would not be too high during the continuous production of superphosphoric acid. As described above, water was sprayed on the duct leading from the hydrator to the scrubber, and cooled acid was recycled to the hydrator. Phosphorus was burned at a rate of 2450 pounds per hour. The air added to the vaporizer and combustion chamber amounted to 175% of that theoretically required for oxidation of the phosphorus. Air added for cooling after the combustion chamber increased the total air used to 300% of that theoretically required for oxidation of the phosphorus. The third column in Table II gives data obtained when the plant was operated in this manner.

There was considerable reduction in the gas temperature throughout that part of the plant constructed of stainless steel—i.e., lower than during normal operation of the plant for production of acid of the usual concentration;

Table II. Acid Plant Operating Data

	Production of Ordinary Acid	Production of Superphosphoric Acid in	
		Original plant	Modified plant <sup>a</sup>
Phosphorus burned, lb./hr.	2157	2600	2450
Temperature, ° F.			
Bottom of combustion chamber	1015	1023	1060
Hydrator outlet	230	309	208
Scrubber inlet	215	234	170
Acid production from Hydrator			
Rate, g.p.m.	5.05	4.65	6.82
Concentration, % P <sub>2</sub> O <sub>5</sub>	65.5	77.0	77.0
P <sub>2</sub> O <sub>5</sub> content, lb./hr.	2940	3540	4967
Temperature, ° F.	460	600	535
Scrubber			
Rate, g.p.m.	5.0	5.15	1.74 <sup>b</sup>
Concentration, % P <sub>2</sub> O <sub>5</sub>	51.4	57.5	49.2
P <sub>2</sub> O <sub>5</sub> content, lb./hr.	1995	2430	642
Temperature, ° F.	212	220	155

<sup>a</sup> Plant modified by addition of cooling water spray to hydrator exhaust duct and by provision for recycling of scrubber acid to hydrator.

<sup>b</sup> Net production; 5.9 g.p.m. were recycled.

for example, gas temperatures were 22° and 45° F. lower, respectively, at the hydrator outlet and the scrubber inlet.

The rate at which acid was recycled from the scrubber to the hydrator was 5.9 gallons per minute. Under these conditions, 88% of the total phosphorus pentoxide was obtained as superphosphoric acid containing 77% phosphorus pentoxide. A small increase in recycle rate would have been necessary for essentially all the production to be superphosphoric acid. In other runs, the concentration and quantity of the acid from the hydrator was such that it could have been mixed with the dilute acid to obtain acid containing 76% phosphorus pentoxide.

With this method of operation, the concentration of the acid recycled to the throat of the scrubber was about the same as that during normal operation of the plant (50% phosphorus pentoxide). The over-all recovery of phosphorus pentoxide in the plant during the production of superphosphoric acid was 99.9%, the same as that obtained in normal operation.

The temperature of the acid draining from the hydrator was 535° F., which is considerably higher than during normal operation of the plant. While this temperature was not too high for a hydrator constructed of carbon, it could not be tolerated in one constructed of stainless steel, such as is used in some plants. In those plants, provisions for extra cooling would have to be made to protect the hydrator from excessive corrosion. One way of lowering the temperature would be to increase the amount of cooled acid recycled to the hydrator. Another way would be to insert a graphite tubular heat exchanger between the combustion chamber and the hydrator, as has been done in several plants (8). The best procedure would depend on the type of plant and the materials of construction.

These tests demonstrated the feasibility of producing superphosphoric acid in an acid plant of standard design. The cost of production of the acid would not be significantly greater per unit of phosphorus pentoxide than that for ordinary acid.

**Possible Uses of the Acid.** As the acid can be readily diluted and hydrolyzed to obtain ordinary acid containing 75% orthophosphoric acid, it should serve the same purposes as such acid as well as offering a number of important advantages. The acid contains about 70% more phosphorus pentoxide per unit of volume than ordinary acid, which should reduce the cost of handling and storage.

Experimental work and tests in large-scale equipment have shown that the acid can be used to produce much more concentrated solid and liquid fertilizers. Phosphate rock was acidulated with the acid in a cone mixer to produce superphosphate with good physical properties that contained up to 55% available phosphorus pentoxide as compared with 48% available phosphorus pentoxide when regular acid was used. In the production of liquid fertilizer, use of the acid, which contains polyphosphoric acids, makes possible the production of solutions of higher concentration than can be made with ordinary phosphoric acid, which contains phosphate in the ortho form only. For instance, 11-33-0 and 11-36-0 liquid fertilizers were produced by ammoniation of the acid (70), whereas 8-24-0 is the most concentrated liquid produced from ordinary acid.

Exploratory tests were made in which 8-24-0 liquid fertilizer was produced by the ammoniation of wet-process phosphoric acid while superphosphoric acid was being added to the extent of 10% of the total phosphorus pentoxide. Less of the impurities in the wet-process acid were precipitated as a result of the sequestering effect of the polyphosphates

present (7). Superphosphoric acid might be used in conjunction with unconcentrated wet-process acid (32% phosphorus pentoxide) to produce liquid fertilizers.

The acid can be used to advantage in the formulation of granular fertilizers. For example, use of the acid in the pilot-plant TVA continuous ammoniator to produce a 5-20-20 grade gave a higher temperature with the result that granulation occurred at a lower moisture content than when conventional acid or concentrated superphosphate was used. Consequently, the moisture content of the product was lower, and the product did not require drying.

TVA is making limited quantities of superphosphoric acid available to fertilizer manufacturers for experimental use in the production of high-analysis liquid and solid fertilizers.

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## BORON FERTILIZATION

### Borosilicate Glass as a Continuing Source of Boron for Alfalfa

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Crop response to residual borosilicate glass and uniformity of boron release from such a glass were evaluated in a greenhouse experiment by growth of alfalfa on Evesboro soil cultures during a second year after treatment. Boron content of the crop was sustained in substantially the same range as that obtained with the newly placed glass in the first year. As application of glass was increased, boron removal by the crop in the 2 years ranged from 142 to 67% of estimated release in the first year alone. Steady release of boron from the particular glass is indicated.

BOROSILICATE GLASSES have been studied (2, 3, 5, 6) to find slowly soluble materials to effect boron fertilization, especially in land areas of coarse-textured soils and heavy rainfall (4). The carrier is used to release boron steadily to compensate for losses from the root zone as they occur during crop growth.

In a 1954 investigation by the authors (2), a coarsely ground borosilicate glass frit released part of its boron in Evesboro sandy loam during an 8-month period in which alfalfa was grown. However, the wide variation in response to boron treatment made it impossible to determine whether or not solubilization from the glass had been, in fact, a gradual process. Therefore, alfalfa was grown on some of the cultures again during the

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following year to evaluate response to the residual glass (boron), and to determine uniformity of release from the glass by comparison of total response in two successive years of crop growth.

#### Experimental Procedure

The cultures (7.5 pounds of soil in No. 10 cans) selected for reseeded to alfalfa contained residuals of minus 20-mesh glass No. 176-C. The original additions of glass, which were thoroughly mixed through the soil, were equivalent in boron to 0, 19, 38, 76, and 152 pounds of borax per acre. The soil, after winter storage in an air-dry condition, was moistened, sieved, and mixed individually with the equivalent of 200 pounds of phosphorus pentoxide and 200 pounds of potassium oxide per acre. The pH prior to the application of supplemental fertilizers was approximately 6.0. The

amount of boron in the tap water added to maintain adequate soil moisture was estimated to be equivalent to about 0.1 pound of borax per harvest.

Ranger alfalfa was planted on May 20, and harvested four times in the following 7 months. The above-ground portion of the plant was dried at 65° C., weighed, and analyzed for boron by the procedure of Dible, Truog, and Berger (7).

#### Effect of Residual on Crop

**Vegetative Response.** General growth of the crop varied more than in the previous season. The yields (Table I), in comparison to those of the year before, were roughly one half in the first two harvests, the same in the third, and double in the fourth. There was, also, greater fluctuation in average growth rate (Table II).