PROPERTIES OF MARKETED FERTILIZERS

Physical and Chemical Characteristics of Mixed Fertilizers and Superphosphates Marketed in 1955–56

Part I. Forms and Solubility of Phosphorus

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Part II. Reaction, Particle Size, and Inert Matter Contents

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The distribution of phosphorus content among the water-soluble, available, and citrateinsoluble forms and information relative to the reaction, particle size, moisture, acidinsoluble ash and carbonate contents, and the acid- or non-acid-forming qualities of mixed fertilizers and superphosphates marketed in the United States during the 1955–56 fertilizer season were obtained and compared with data derived from a similar survey of fertilizers marketed in 1949–50. The portion of the total phosphorus in water-soluble form decreased from 46.9% in 1949–50 to 43.4% in 1955–56; the water-soluble portion of the available phosphorus decreased from 50.2 to 45.8%. In both periods the acidinsoluble ash and the calcium carbonate equivalent added as make-weight material or partially to offset the acid-forming character of mixed fertilizers amounted to approximately one eighth of the average fertilizer.

S OLID MIXED FERTILIZERS and super-phosphates marketed in the United States during the 1955-56 fertilizer year were surveyed for the purpose of obtaining information on some of their physical and chemical characteristics. These papers present data on the distribution of the phosphorus content among the water-soluble, available, and citrateinsoluble forms and information relative to the reaction, particle size and moisture, acid-insoluble ash and carbonate contents, and the acid- or non-acidforming qualities of mixed fertilizers and superphosphates by regions. They compare the results with data obtained in a similar survey of fertilizers marketed in 1949-50 (4, 5).

Design of Survey

To make the survey as representative as possible, the selection of mixed fertilizer samples from each major geographical region was based on the tonnage of the several grades marketed and the production of individual manufacturers. Scholl, Wallace, and Fox (7) reported that 97% of the 15,258,053

¹ Present address, University of Michigan, Ann Arbor, Mich. tons of mixtures consumed in 1953–54, the latest season for which data then were available, represented 176 different grades marketed in excess of 2500 tons each. In general, the 15 principal grades in each region were sampled in proportion to their marketed tonnage on the basis of one sample for each 30,000 tons. At least one sample was selected, however, for each such grade marketed in excess of 15,000 tons. Where additional samples were required, random selections were made from among grades marketed in excess of 2500 tons each.

Owing to the limited number of samples required for the West, South Central, Mountain, and Pacific regions, random selection of samples was made from among the principal grades on the basis of one sample for each 30,000 tons of mixtures marketed.

Estimates of the relative marketings of the several manufacturers in each region were derived largely from the number of official inspection samples drawn for each manufacturer as indicated by state fertilizer reports. The number of samples selected to represent each manufacturer then was based on one sample for each 30,000 tons of estimated marketings. Random selection of samples from additional manufacturers was made to provide the desired number of samples from the particular region,

On the basis of the above consideration state control officials were requested to supply, where possible, unground official inspection samples of specified grades of mixtures marketed by specified manufacturers. In some instances unground samples were not available, and in others the desired grade either could not be supplied as the product of the specified manufacturer or could not be supplied at all. In such cases the control official was asked to supply ground samples representing the desired grade and manufacturer, the desired grade marketed by another manufacturer, a randomly selected grade marketed by the initially selected manufacturer, or a grade representing both random selection of grade and manufacturer.

In addition, each control official was asked to supply for comparison three or four samples of superphosphate randomly selected as to grade and manufacturer.

State fertilizer control officials of 35 states cooperated by supplying 491 official inspection samples of mixed fertilizers representing 90 grades, 60 plant-nutrient ratios, and 160 manufacturers. Two hundred thirty-nine or nearly 49% of the samples represented products marketed by 10 manufacturers. Five of the 491 samples represented N-K mixtures marketed in four grades and three plant-nutrient ratios by five manufacturers in four states of the South Atlantic region. The products of one of these manufacturers were not otherwise represented in the survey. Seventeen of the plant-nutrient ratios were represented by 47 grades and a total of 356 or 72.5%of the samples.

Thirty states supplied 103 official inspection samples of nine grades of superphosphate marketed by 54 manufacturers. Seventy-five samples represented three grades of normal superphosphate (18 to 20%) marketed in 26 states by 41 manufacturers and 28 represented six grades of concentrated superphosphate (42 to 49%) marketed in 12 states by 17 manufacturers. Thirtyone superphosphates represented products of 22 manufacturers not otherwise represented in the survey.

Distribution of both superphosphates and mixed fertilizers by regions in relation to the numbers of states, samples, grades, plant-nutrient ratios, and manufacturers is presented in Table I. Table II shows the distribution of samples among the P, N-P, N-K, P-K, and N-P-K classifications in relation to the number of manufacturers and the number of samples representing each manufacturer. Approximately one third of the superphosphates and one third of the mixed fertilizers collected were the products of 4-12-12, 4-8-6, 4-8-8, 5-10-10, 6-12-12, 4-10-6, 4-10-7, 4-16-16, 5-20-20, 5-10-5, and 10-10-10 representing 11 nutrient ratios-were represented by at least 10 samples each for a total of 322 or nearly two thirds of the 486 phosphorus-containing mixtures.

PART I. FORMS AND SOLUBILITY OF PHOSPHORUS

Analytical Methods

Total, water-soluble, and citrate-insoluble P_2O_5 contents of the super-

phosphates and mixtures were determined in accordance with official methods of analysis adopted by the Association of Official Agricultural Chemists (2). As requested, nearly 80% of the mixtures were supplied in the unground condition. In these cases analyses were conducted on freshly ground portions of the samples.

Results. In agreement with earlier surveys, wider variations and lower mean values were observed in the water-soluble and in the available (total minus citrateinsoluble) portions of the total phosphorus in mixtures than in superphosphates. Analytical data for each region are summarized in Table III in relation to superphosphates and to classes of mixtures.

Water-Soluble Portion of Total Phosphorus. The average value for the water-soluble portion of the total P_2O_5 content of the superphosphates is substantially the same as in the 1949–50 survey (5). The averages for the N–P, N–P–K, and all mixtures are 3.1 to 4.2 percentage units lower and the average for the P–K mixtures 17.1 units higher.

Available Portion of Total Phosphorus. In comparison with the 1949– 50 survey, the average values for superphosphates and N-P mixtures are substantially the same and those for P-K, N-P-K, and all mixtures from 1.3 to 2.0 percentage units higher.

Water-Soluble Portion of Available Phosphorus. In relation to the 1949-

| Table I. | Distribution of Samples in Relation to Region and Numbers of States, | Grades, | Plant-Nutrient | Ratios, | and |
|----------|--|---------|-----------------------|---------|-----|
| | Manufacturers | | | | |

| | | | | | | | | | Mixe | d Fertilizers | ; | | |
|------------------|--------|--------|-----------|-----------|---------|--------|-----|--------|----------------|---------------|----------|-----------|---------|
| | | Su | perphospl | hates | | | | | | | Plant- | | _ |
| | | Gro | ades | Manu- | | | | Grades | | | nutrient | Manu- | |
| Region | States | Normal | Concd. | facturers | Samples | States | N-P | N-K | Р-К | N-P-K | ratios | facturers | Samples |
| | | | | | | Numbe | er | | | | | | |
| New England | 3 | 2 | 1 | 9 | 12 | 3 | | | 2 | 12 | 10 | 13 | 16 |
| Middle Atlantic | 6 | 2 | | 14 | 21 | 5 | | | $\overline{2}$ | 17 | 13 | 26 | 59 |
| South Atlantic | 4 | 2 | 1 | 9 | 12 | 5 | | 4 | 3 | 36 | 30 | 64 | 168 |
| East North Cen- | | | | | | | | | | | | | |
| tral | 3 | 2 | | 10 | 12 | 5 | | | 3 | 13 | 10 | 31 | 111 |
| West North Cent. | 5 | 2 | 3 | 16 | 19 | 5 | 4 | | 2 | 19 | 14 | 29 | 47 |
| East South Cent. | 3 | 1 | 2 | 8 | 10 | 4 | | | 1 | 15 | 13 | 28 | 62 |
| West South Cent. | 1 | 1 | 2 | 4 | 4 | 3 | | | | 10 | 7 | 12 | 14 |
| Mountain | 4 | 2 | 4 | 6 | 12 | 4 | 3 | | | 3 | 6 | 8 | 10 |
| Pacific | 1 | 1 | | 1 | 1 | 1 | 2 | | | 2 | 3 | 3 | 4 |
| U. S. | 30 | 3 | 6 | 54 | 103 | 35 | 9 | 4 | 6 | 71 | 60 | 160 | 491 |

| Table II. | Distribution | of | Samples | in | Relation | to | Manufacturers |
|-----------|--------------|----|---------|----|----------|----|---------------|
| | | | | | | | |

| | Superphosphates | | | | | | | Mixed Fertilizers | | | | | | | | |
|---------------------------------------|-------------------------|--------------|-------------------------|-----------------|-------------------------|--------------|-------------------------|-------------------|-------------------------|--------------|-------------------------|--------------|-------------------------|--------------|-------------------------|--------------|
| | Normal | | Concentrated | | All | | N-P | | N-K | | P-K | | N-P-K | | All | |
| No. of Samples per Manufacturer | Manu- fac- turers | Sam- ples | Manu- fac- turers | Sam- ples | Manu- fac- turers | Sam- ples | Manu- fac- turers | Sam- ples | Manu- fac- turers | Sam- ples | Manu- fac- turers | Sam- ples | Manu- fac- turers | Sam- ples | Manu- fac- turers | Sam- ples |
| | | | | | | | Nur | nber | | | | | | | | |
| 1 | 27 | 27 | 8 | 8 | 35 | 35 | 13 | 13 | 5 | 5 | 12 | 12 | 94 | 94 | 102 | 102 |
| 2 | 7 | 13 | 5 | 9 | 11 | 22 | 2 | 4 | | | 5 | 10 | 26 | 52 | 30 | 60 |
| 3 | 1 | 3 | 1 | 3 | 2 | 6 | | | | | | | 5 | 15 | 6 | 18 |
| 4 | • • | • • | | • • | | | | | | | 1 | 4 | 3 | 12 | 1 | 4 |
| 5 | 1 | 3 | 1 | 2 | 1 | 5 | | | | | | | 4 | 20 | 6 | 30 |
| 6-10 | 5 | 29 | 2 | 6 | 5 | 35 | | | | | | | 5 | 40 | 5 | 38 |
| 11-20 | | | | | | | | | | | | | 3 | 37 | 4 | 49 |
| >20 | | | | | | | | | | | | | 6 | 173 | 6 | 190 |
| Total | 4 1 | 75 | 17 | $2\overline{8}$ | 54ª | 103 | 15 | $\overline{17}$ | 5 | 5 | 18 | 26 | 146 | 443 | $\overline{160}b$ | 491 |

^a 32 manufacturers marketed 72 superphosphates and 282 mixtures; 22 marketed 31 superphosphates but no mixtures. ^b 128 manufacturers marketed 209 mixtures but no superphosphates. 50 survey the average value for the water-soluble portion of the available P_2O_5 of superphosphates is substantially identical. The averages for the N-P, N-P-K, and all mixtures are 3.0 to 5.2 percentage units lower, and the average for the P-K mixtures 16.9 units higher.

Relative Solubility and Availability of Phosphorus in Superphosphates and in Mixtures

A greater proportion of the available P_2O_5 is present in water-soluble form in superphosphates than in mixed fertilizers. Similarly, a greater proportion of the

total P_2O_5 is present in available form in superphosphates than in mixtures.

The solubility and availability characteristics of the P_2O_5 differed appreciably among the various superphosphates and mixtures as well as between the two classes of materials themselves. The

Table III. Total Phosphorus and Portion of Total Phosphorus in Water-Soluble and in Available Form, and of Available Phosphorus in Water-Soluble Form

| | | _ | | | ortion of To | Portion of Available P ₂ O ₅ | | | |
|---------------------------------------|-----------|------------------------|--------------|------------------------|--------------|--|--------------|------------------------|--------------------------|
| | No. of | Total P2O | 5, % | Water-Solub | le Form | Available | Form | in Water-Soluble | e Form, 🕉 |
| Region and Item | Samples | Range | Mean | Range | Mean | Range | Mean | Range | Mean |
| New England | | | | | | | | | |
| All superphosphates, 18-46% | 12 | 18.7-46.7 | 22.7 | 72.6-92.2 | 83.3 | 96.1-99.6 | 98.0 | 75.0-92.9 | 85.0 |
| Superphosphate, $18-20\%$ | 11 | 18.7-22.1 | 20.5 | 72.6-89.8 | 82.5 | 96.1-99.6 | 97.9 | 75.0-90.1 | 84.3 |
| Superphosphate, 46% | 16 | e 2 16 0 | 46.7 | 15 7 00 2 | 92.2 | 04 1 00 1 | 99.2 | 16 2 02 6 | 92.9 |
| P_K grades | 10 | 14 5-16 9 | 11.5 | 15.7-82.5 | 41.5 | 94.1-99.1 | 90.0 | 10.2-83.0 | 42.8 |
| N-P-K grades | 14 | 8 2-15 5 | 10.7 | 15 7 - 54 7 | 36.0 | 94 1-99 1 | 96.4 | 16 2-56 3 | 37 4 |
| Middle Atlantic | | 0.2 15.5 | 10.7 | 19.7 94.7 | 50.0 | 24.1 <i>))</i> .1 | 20.1 | 10.2 50.5 | 57.1 |
| All superphosphates, 18-20% | 21 | 19.0-22.9 | 21.5 | 61.9-90.1 | 81.4 | 87.6-99.8 | 96.3 | 70.7-94.0 | 84.3 |
| Superphosphate, 18-20% | 21 | 19.0-22.9 | 21.5 | 61.9-90.1 | 81.4 | 87.6-99.8 | 96.3 | 70.7-94.0 | 84.3 |
| All mixtures ^a | 59 | 6.2-21.5 | 11.8 | 10.9-79.6 | 46.1 | 84.3-99.2 | 94.7 | 11.2-81.3 | 48.4 |
| P–K grades | 3 | 15.6-21.5 | 19.4 | 63.8-79.6 | 71.8 | 95.7-98.0 | 96.6 | 66.4-81.3 | 74.2 |
| N-P-K grades | 56 | 6.2-16.6 | 11.4 | 10.9-77.7 | 44.7 | 84.3-99.2 | 94.6 | 11.2-80.0 | 47.1 |
| South Atlantic | 10 | 17 0 40 0 | 22.0 | (0, 2, 00, 0 | 01.0 | 04 0 00 0 | 07 (| (1 0 02 (| 02 1 |
| All superphosphates, $18-2007$ | 12 | 17.8-48.0 | 22.9 | 60.2 - 90.0 | 81.2 | 94.9-99.8 | 97.6 | 61.9 - 92.6 | 83.1 |
| Superphosphate, 16-20% | 1 | 17.0422.5 | 48.0 | 00.2-90.0 | 84 8 | 94,9-99,0 | 97.5 | 01.9-92.0 | 85.0 |
| All mixtures ^a | 163 | 31-204 | 10.3 | 5 6-96 0 | 38 6 | 48 9-99 6 | 93.6 | 6 2-97 0 | 41 1 |
| P-K grades | | 13.0-20.0 | 15.4 | 64.1-81.3 | 71.4 | 94 1-97 8 | 96.2 | 67.3-84.2 | 74.3 |
| N–P-K grades | 158 | 3.1-20.4 | 10.1 | 5.6-96.0 | 37.6 | 48.9-99.6 | 93.5 | 6.2-97.0 | 40.1 |
| East North Central | | | | | | | | | |
| All superphosphates, 18-20% | 12 | 18.5-22.2 | 21.1 | 34.2-88.1 | 77.0 | 95.1–99.8 | 97.0 | 35.6-88.3 | 79.2 |
| Superphosphate, 18–20% | 12 | 18.5-22.2 | 21.1 | 34.2-88.1 | 77.0 | 95.1–99.8 | 97.0 | 35.6-88.3 | 79.2 |
| All mixtures ^a | 111 | 6.7-23.4 | 14.2 | 10.4-81.3 | 48.6 | 86.0-99.9 | 95.4 | 11.0-83.1 | 50.8 |
| P-K grades | 102 | 10.3-23.4 | 18,6 | 39.5-81.3 | 65.8 | 94.7-99.0 | 96.9 | 40.9-83.1 | 67.9 |
| West North Central | 105 | 6.7-21.6 | 15.9 | 10.4-/9./ | 4/.3 | 86.0-99.9 | 95.3 | 11.0-81.3 | 49.4 |
| All superphosphates 18-48% | 19 | 19 3-49 6 | 30 1 | 78 0-94 4 | 86 3 | 02 1_00 0 | 97.0 | 81 4-97 9 | 88 8 |
| Superphosphate 18–20% | 6 | 19.3 - 22.2 | 21^{0} | 80 2-94 4 | 86.5 | 92.1-99.9 92.1-99.9 | 96.6 | 81 4-97 9 | 89.5 |
| Superphosphate, 42–48% | 13 | 44.7-49.6 | 47.5 | 78.0-91 6 | 86 2 | 94 1-99.7 | 97.2 | 81.6-94.1 | 88.5 |
| All mixtures | 47 | 9.6-34.9 | 18.4 | 4.0-87.0 | 52.7 | 73,6-99.9 | 94.3 | 4.4-90.8 | 55.5 |
| N–P grades | 9 | 16.1-34.9 | 24.8 | 48.6-77.8 | 58.3 | 87.6-98.2 | 94.4 | 51.0-79.8 | 61.7 |
| P-K grades | 4 | 19.2–21.9 | 20.9 | 68.7-84.0 | 78.3 | 92.8–99.4 | 96.6 | 74.0-85.4 | 81.0 |
| N-P-K grades | 34 | 9.6–26.2 | 16.4 | 4.0-87.0 | 48.3 | 73.6-99.9 | 94.0 | 4.4-90.8 | 50.8 |
| East South Central | 4.0 | 00 0 51 1 | a () | 74 0 00 4 | 0.0 | 05 0 00 (| 00.0 | 77 4 02 0 | 05.4 |
| All superphosphates, $20-49\%$ | 10 | 20.2-51.1 | 26.8 | 74.2-93.4 | 83.5 | 95.9-99.6 | 98.0 | 77.4-93.8 | 85.1 |
| Superphosphate, 20% | 2 | 20.2-22.7 45.7-51.1 | 21.4 19.1 | 74.2-87.0 80.8-03.4 | 02.0 97.1 | 95,9-99,5 | 97.7 | 77.4-88.9 81.4-03.8 | 04.3 97.6 |
| All mixtures ^a | 62 | 7 7-14 8 | 11 2 | 0.7 - 84.1 | 32.8 | 73 2-09 3 | 99.4 | 01.4-95.0 0.9-84.7 | 34 0 |
| P-K grades | 4 | 14.3-14.8 | 14.6 | 56.0-84 1 | 72.5 | 97 3-99 3 | 98.0 | 57.2-84.7 | 73 9 |
| N-P-K grades | 58 | 7.7-14.7 | 10.9 | 0.7-65.9 | 30.1 | 73,2-97.1 | 92.7 | 0.9-68.1 | 32.2 |
| West South Čentral | | | | | | | | | |
| All superphosphates, 20-48% | 4 | 21.9-51.4 | 42.1 | 81.7-92.2 | 86.9 | 95.3–99.3 | 96.7 | 85.8-92.9 | 89.9 |
| Superphosphate, 20% | 1 | (= à`÷4 4 | 21.9 | | 81.7 | | 95.3 | | 85.8 |
| Superphosphate, 45–48% | 3 | 4/.3-51.4 | 48.8 | 86.3-92.2 | 88.7 | 95.6-99.3 | 97.1 | 90,3-92.9 | 91.3 |
| All mixtures ^o | 14 | 8.9-21.4 | 21.5 | 9.8-74.8 | 43.0 | 89.8-97.8 | 94.5 | 10.5-77.1 | 45.5 |
| N-P-K grades | 13 | 8 9-21 4 | 11 7 | 9 8-67 4 | 40.6 | 80 8-07 8 | 97.1 | 10 3-69 1 | 42.8 |
| Mountain | 15 | 0.7 21.1 | 11.7 | 2.0 07.4 | 40.0 | 07.0 77.0 | 21.5 | 10.5 07.1 | 72.0 |
| All superphosphates, 19–46% | 12 | 20.4-48.6 | 38.0 | 61,3-87,2 | 78.4 | 70,9-99,5 | 93.3 | 70,1-90,5 | 84.1 |
| Superphosphate, 19-20% | 4 | 20.4–23.3 | 22.1 | 61.3-85.7 | 76.1 | 70.9-99.5 | 87.7 | 85.2-89.5 | 86.8 |
| Superphosphate, 42–46 $\%$ | 8 | 43.0–48.6 | 46.0 | 66.6-87.2 | 79.5 | 91.1-98.8 | 96.1 | 70.1–90.5 | 82.8 |
| All mixtures ^b | 10 | 10.8-25.9 | 18.5 | 11.9-81.6 | 58.6 | 81.0-98.1 | 93.4 | 14.6-86.8 | 61.8 |
| N-P grades | 5 | 10.8-25.9 | 22.3 | 42.9-81.6 | 68.6 | 94.0-94.8 | 94.4 | 45,2-86.8 | 72.6 |
| N-P-K grades | 5 | 11.8-17.0 | 14./ | 11.9-79.8 | 48.7 | 81.0-98.1 | 92.3 | 14.6-81.7 | 51.0 |
| All superphosphates 1907 | 1 | | 20.4 | | 83 7 | | 97.0 | | 85 5 |
| Superphosphate 19% | 1 | | 20.4 | • • • | 83.7 | | 97.9 | | 85 5 |
| All mixtures ^b | 4 | 7.7-10.4 | 8.9 | 76.2-93.1 | 85.1 | 96.7-99.4 | 98.5 | 78.7-93.6 | 86.3 |
| N-P grades | 2 | 7.1-10.2 | 8.7 | 84.0-93.1 | 88.5 | | 99.4 | 84.5-93.6 | 89.1 |
| N-P-K grades | 2 | 7.7-10.4 | 9.1 | 76.2-87.1 | 81.6 | 96.7-98.5 | 97.6 | 78.7-88.4 | 83.6 |
| United States | 107 | 47 0 54 4 | | | | 70 0 00 0 | o | 27 / 27 2 | o |
| All superphosphates, 18-49% | 103 | 17.8-51.4 | 28.2 | 34.2-94.4 | 82.1 | 70.9-99.9 | 96.7 | 35,6-97,9 | 84.8 |
| Superphosphate, 18–20% | /5 | 17.8-23.3 | 21.1 47 2 | 54.2-94.4 66.6.02.4 | 81.1 | /0.9-99.9 | 90.5 07 5 | 33,0-97,9 70,1,04,1 | 83.9 97 1 |
| All mixtures | ∠ð 484 | +3.0-51.4 3.1-34.0 | 47.5 | 0.0-93.4 | 03.U 43.4 | <u>48 0-00 0</u> | 94 2 | 0.1-94.1 0.9-07 0 | 45 8 |
| N-P grades | 17 | 7 1-34 9 | 21 9 | 42 9-93 1 | | 87 6-99 4 | 95.1 | 45.2-93.6 | - 5.8 69.0 |
| P-K grades | 26 | 10.3-23.4 | 17.6 | 39.5-84.1 | 71.6 | 92.8-99.4 | 97.0 | 40.9-85.4 | 73.8 |
| N-P-K grades | 443 | 3.1-26.2 | 11.8 | 0.7-96.0 | 40.9 | 48.9-99.9 | 94.1 | 0.9-97.0 | 43.2 |
| ^a No N-P grades collected. | | | | | | | | | |
| ^b No P-K grades collected. | | | | | | | | | |

distribution of the superphosphates and mixtures in relation to degrees of solubility and availability of their P2O5 contents is shown in Table IV. Approximately 90% of the superphosphates in comparison to 55% of the mixtures contained 95% or more of the total P_2O_5 in available form. In the 1949-50 survey, these percentages were 78 and 38%, respectively. Similarly, the available portion of the P_2O_5 exceeded 90% in 97.1% of the superphosphates (97.8% in 1949-50), and in 91.7% of the mixtures (86.2% in 1949-50). Slightly more than 85% of the superphosphates (90% in 1949-50) but only 5.1% of the mixtures (7.4% in 1949-50) contained 80% or more of the available P2O5 in water-soluble form. Only one of the superphosphates (none in 1949-50) contained less than 50% of the available P_2O_5 in water-soluble form, whereas in 54.7% of the mixtures (49.0% in 1949–50) less than 50% of the available P_2O_5 was water-soluble. The percentage of mixtures containing less than 30% of the available P_2O_5 in water-soluble increased from 15.2 in 1949–50 to 25.4% in 1955–56, an increase of approximately 67%.

The lower values for water solubility and availability of the P_2O_5 exhibited in the 1949–50 survey (5) were attributed to formulation practices involving ammoniation, and incorporation of considerable quantities of liming materials to offset the acid-forming properties of other ingredients and as make-weight material. Changes in these formulation practices between 1949–50 and 1955–56 largely involved increased use of granulation and drying operations with the use of less limestone in relation to P_2O_5 content in the formulation of granular mixtures, continuous ammoniation, sulfuric and (or) phosphoric acid in the formula to permit greater use of nitrogen solutions, and nitric acid in the production of available phosphates. The increased use of phosphoric acid and the decreased use of limestone in certain formulations tend to favor increased water solubility and availability of the phosphorus content. As compared with 1949-50, the average fertilizer in 1955-56, however, exhibited slightly greater phosphorus availability but lower water solubility in relation to both total and available $P_2O_{\,5\cdot}$

Adams and Scholl (7) reported that superphosphates supplied 97.6% of the P_2O_5 content of mixed fertilizers manufactured in 1954. Neglecting the effect of differences in the initial degrees of

| Water-Soluble | Available Portion of Total $P_{2}O_{3}$, Range, $\%$ | | | | | | | | | | | | | | |
|-----------------------------|---|--|---------------|---------------|-----------|-------------------|--------------|-------|--|--|--|--|--|--|--|
| Portion of | 40.0-49.9 | 50.0-59.9 | 60.0-69.9 | 70.0-79.9 | 80.0-89.9 | 90.0-94.9 | 95.0-100.0 | Total | | | | | | | |
| Available P2O5, Range, % | | % of Total Samples in Indicated Ranges | | | | | | | | | | | | | |
| | | | Sup | erphosphates | | | | | | | | | | | |
| 35.0-39.9 | | | | • • • | | | 1.0 | 1.0 | | | | | | | |
| 60.0-69.9 | | | | | : : : | | 1.9 | 1.9 | | | | | | | |
| 70.0-79.9 | | • • • | | | 1.0 | 1.0 | 9.7 | 11./ | | | | | | | |
| 80.0-84.9 | | | | | 1.0 | 1.9 | 21.4 | 23.3 | | | | | | | |
| 00.0-09.9 | • • • | • • • | • • • | 1.0 | 1.0 | 2.9 | 57,9 18 / | 44.7 | | | | | | | |
| 90.0-100.0 | • • • | | | 1.0 | 1.0 | $\frac{1.0}{6.0}$ | 10.4 | 100.0 | | | | | | | |
| Total | | | | 1.0 | 1.9 | 6.8 | 90.5 | 100.0 | | | | | | | |
| | | | | Mixtures | | | | | | | | | | | |
| 0-9.9 | | | | 0.2 | | 0.8 | 1.0 | 2.1 | | | | | | | |
| 10.0-19.9 | | | | 0.4 | 1.6 | 3.3 | 4,1 | 9.5 | | | | | | | |
| 20.0-29.9 | | 0.2 | | 0.4 | 1.4 | 6.8 | 4.9 | 13.8 | | | | | | | |
| 30.0-39.9 | | 0.2 | | 0.2 | 1.0 | 4.3 | 6.8 | 12.6 | | | | | | | |
| 40.0-49.9 | 0.2 | | 0.2 | 0.2 | 0.6 | 7.4 | 8.0 | 16.7 | | | | | | | |
| 50.0-59.9 | | | 0.2 | | 1.0 | 7.8 | 12.8 | 21.8 | | | | | | | |
| 60.0-69.9 | | | • • • | | • • • | 4.1 | 8.6 | 12.8 | | | | | | | |
| 70.0-79.9 | • • • | | • • • | | • • • | 0.8 | 4.9 | 5.0 | | | | | | | |
| 90.0-100.0 | | | | · · · | | 0.8 | 0.6 | | | | | | | | |
| Tetal | 0.2 | 0.4 | $\frac{1}{0}$ | $\frac{1}{1}$ | 5 9 | 26 4 | 55.2 | 100.0 | | | | | | | |
| TOTAL | 0.2 | 0.4 | 0.4 | 1.4 | 5.0 | 50.4 | 55,5 | 100.0 | | | | | | | |

Table IV. Distribution of Samples in Relation to Solubility and Availability of Phosphorus

Table V. Distribution of Total Phosphorus in Water-Soluble and in Available Form in Relation to 16 Principal Grades

| | | No. of | | Portion of To | Portion of Available P ₂ O ₅ | | | | |
|------------------|---------|-----------|--------------|---------------|--|------|------------------------|------|--|
| Grade | No. af | Manu- | Water-Solubl | e Form | Available I | orm | in Water-Soluble Form, | | |
| N-P205K-20 | Samples | facturers | Range | Mean | Range | Mean | Range | Меал | |
| 4-10-6 | 16 | 13 | 13.7-57.8 | 26.6 | 91.6-98.3 | 95.2 | 14.5-59.7 | 27.9 | |
| 4-10-7 | 16 | 13 | 14.7-48.3 | 28.1 | 89.1-96.0 | 93.6 | 16.0-53.0 | 30.1 | |
| 4-8-8 | 14 | 13 | 5.6-76.2 | 28.8 | 64.7-98.1 | 92.0 | 6.2-77.9 | 31.4 | |
| 4-8-6 | 10 | 10 | 7.7-58.1 | 30.0 | 91,1-97,4 | 94.4 | 8.0-61.4 | 31.8 | |
| 5-10-5 | 21 | 15 | 10.1-70.4 | 36.2 | 90,2-99.1 | 94.1 | 11,2-71,1 | 38.3 | |
| 3-9-6 | 27 | 18 | 6.5-68.5 | 37.5 | 73,2-98.5 | 92.7 | 6.7-69.8 | 40.1 | |
| 4-12-12 | 14 | 13 | 18.4-68.7 | 40.2 | 86.9-97.3 | 94.3 | 19.4-70.8 | 42.6 | |
| 5-10-10 | 43 | 26 | 10.4-77.7 | 41.0 | 84.3-99.2 | 94.7 | 11.0-80.0 | 43.1 | |
| 3-9-9 | 19 | 15 | 18.8-62.7 | 42.2 | 89.7-98.0 | 94.7 | 19.7-64.1 | 44.6 | |
| 10-10-10 | 21 | 15 | 19.7 - 78.6 | 44.5 | 86,9-99.2 | 96.0 | 22,7-81,3 | 46.2 | |
| 3-12-12 | 54 | 31 | 4.0-70.3 | 44.1 | 73.6-99.9 | 94.4 | 4.4-72.6 | 46.5 | |
| 2-12-12 | 13 | 12 | 34.7-57.5 | 48.6 | 92.2-98.0 | 95.4 | 35.6-59.6 | 50.9 | |
| 6-12-12 | 10 | 4 | 27.6-71.3 | 52.9 | 90.2-97.4 | 94.8 | 29.7-74.5 | 55.6 | |
| 4-16-16 | 23 | 16 | 15.1-81.3 | 53.2 | 88.4-99.1 | 94.8 | 17.1-83.0 | 55.8 | |
| 5-20-20 | 10 | 9 | 29.5-74.0 | 57.4 | 96.0-98.6 | 97.1 | 30.1-75.0 | 59.1 | |
| 0-20-20 | 11 | 9 | 39.5-84.0 | 72.2 | 92.8-99.4 | 96.8 | 40.9-85.4 | 74.5 | |
| Total, 16 grades | 322 | 113 | 4.0-84.0 | 42.1 | 64.7-99.9 | 94.5 | 4,4-85,4 | 44.3 | |
| 70 other grades | 164 | 83 | 0.7-96.0 | 46.1 | 48.9-99.9 | 93.9 | 0.9-97.0 | 48.7 | |
| Total | 486 | 159 | 0.7-96.0 | 43.4 | 48.9-99.9 | 94.3 | 0.9-97.0 | 45.8 | |

availability of superphosphates and the minor sources of phosphorus in mixed fertilizers, an average of 97.5% (96.1% in 1949–50) of the originally available P_2O_5 remained in available form after formulation of the mixtures, whereas only 52.9% (57.3% in 1949–50) of the water-soluble P_2O_5 was still water soluble.

Regional averages for the available portion of the total P2O5 remaining in available form ranged from 94.9% for the East South Central region to slightly more than 100% for the Mountain and Pacific areas. Similarly, regional averages for the water-soluble portion of the total P2O5 remaining in water-soluble form ranged from 39.3% for the East South Central region to more than 100%for the Pacific area. Regional averages for the water-soluble portion of the available P2O5 remaining in water-soluble form ranged from 41.0 to 100.9% and averaged 54.0% in comparison to 59.4%in 1949–50.

In general, higher averages for both water solubility and availability of the P_2O_5 contents of the mixtures were observed for those regions in which a greater proportion of the phosphate supply is available as concentrated superphosphate or in forms other than superphosphate. The lower average values were associated with regions in which ammoniation and formulation of physiologically neutral mixtures are more extensively practiced. Intermediate values were associated with the East North Central and West North Central regions.

Principal Mixed Fertilizer Grades

Data on the distribution of P_2O_5 between water-soluble and available forms are summarized in Table V. Although considerable variation exists for each grade in the distribution of P_2O_5 between water-soluble and available forms, listing these grades in the ascending order of the average percentages of total P_2O_5 in water-soluble form requires only the interchange of the 3–12– 12 and 10–10–10 grades. Four of the 11 principal grades in the 1949–50 survey— 2–12–6, 3–12–6, 4–12–4, and 6–8–4were not classified among the 16 principal grades in the current survey.

The general tendency is for the watersoluble fraction of the total and of the available $P_{9}O_{5}$ to increase as the N-P₉O₅ ratio decreases, and in the case of the higher analysis mixtures to increase as the P_2O_5 grade of the mixture increases. These relationships reflect the economic pressure on manufacturers to derive a high proportion of the total nitrogen from relatively inexpensive ammoniating solutions. With solutions now available and particularly in connection with the use of supplemental acid as an aid in granulation processes all of the nitrogen for these grades may be supplied in solution form.

Grades in Relation to Nitrogen Content

In Table VI data are summarized in relation to the principal nitrogen grades of the mixtures. Of the 16 nitrogen grades included in the survey, the grades between 0 and 10% N represented 96.5% or 469 of the 486 samples. The total P_2O_5 in water-soluble and in available form in superphosphate decreases appreciably in the formulation of N-P-K

mixtures. The water solubility of the phosphorus in the P-K mixtures also decreased appreciably, but to a much lesser degree than indicated by the 1949–50 data. Presumably in the case of the P-K mixtures the observed decrease resulted largely from incorporation of liming materials.

The 4, 5, and 6% N grades exhibit lower values for the portion of the total P_2O_5 in water-soluble and in available form and for the portion of the available P_2O_5 in water-soluble form than either higher or lower N grades. The 5% N grade, however, shows higher values for water-solubility and availability than the 4 and 6% grades. The data indicate that in general the P_2O_5 contents are subjected to higher rates of ammoniation in the formulation of 4, 5, and 6% N grades than in the formulation of the other grades.

Relative Solubility of Phosphorus in Commercial Solid Mixed Fertilizers, 1880–1956

The relative solubility and availability of the P_2O_5 content of phosphorus containing solid commercial mixed fertilizers as determined in the present



Table VI. Distribution of Total Phosphorus in Water-Soluble and in Available Form in Relation to Nitrogen Grade

| | | | No. of | | Po | rtion of Tol | al P_2O_5 , % | | Portion of Availe | able P2O5 | |
|--------------------------------|---------|--------|----------|-------------------------|---------------|--------------|-----------------|------|--------------------------|-----------|--|
| N Grade | No. of | No. of | Manufac- | Weighted Average Grade. | Water-Soluble | e Form | Available F | orm | in Water-Soluble Form, % | | |
| % | Samples | Grades | turers | $N-P_2O_5-K_2O, \%$ | Range | Mean | Range | Mean | Range | Mean | |
| 0 | 26 | 6 | 18 | 0-16,65-18,15 | 39.5-84.1 | 73.4 | 92.8-99.4 | 97.3 | 40.9-85.4 | 73.8 | |
| 2 | 15 | 2 | 14 | 2-12.00-11.20 | 16.8-57.5 | 51,0 | 78.5-98.0 | 96.1 | 21.4-59.6 | 48.4 | |
| 3 | 121 | 8 | 51 | 3-10.69-10.61 | 4.0-70.3 | 44.8 | 73.2-99.9 | 95.2 | 4,4–72.6 | 45.4 | |
| 4 | 116 | 15 | 57 | 4-11,15-9,27 | 5.6-81.3 | 37,8 | 48.9-99.1 | 94.7 | 6,2-83.0 | 39.3 | |
| 5 | 83 | 10 | 45 | 5-11.20-9.90 | 10.1-77.7 | 43,9 | 54.2-99.2 | 93.8 | 11.0~80.0 | 43.6 | |
| 6 | 49 | 15 | 30 | 6-10.12-7.53 | 0.7 - 78.1 | 33.1 | 61.0-98.1 | 94.8 | 0.9-82.5 | 36.7 | |
| 8 | 23 | 11 | 17 | 8-14.43-8.61 | 9.8–87.1 | 51.2 | 89.5-99.6 | 96.0 | 10.3-88.4 | 51.1 | |
| 10 | 36 | 9 | 24 | 10-12.50-7.94 | 19,4-96.0 | 49.9 | 86.9-99.2 | 96.7 | 19.9-97.0 | 52.9 | |
| Subtotal | 469 | 76 | 152 | 4.50-11.53-9.96 | 0.7-96.0 | 42.8 | 48.9–99.9 | 94.2 | 0.9-97.0 | 45.2 | |
| Eight other N | | | | | | | | | | | |
| grades | 17 | 10 | 14 | 12.76-12.12-7.29 | 16.3-93.1 | 62.0 | 94.1–99.9 | 96.9 | 16.8–93.6 | 62.0 | |
| $\operatorname{\check{T}otal}$ | 486 | 86 | 159 | 4.59-11.55-9.87 | 0.7-96.0 | 44.5 | 48.9-99.9 | 95.3 | 0.9-97.0 | 45.8 | |

survey is compared with similar information covering the period 1880-1950 (5) (Figure 1). Although the data for the years prior to 1949-50 probably are not as completely representative of the entire country as those obtained in the 1949-50 and 1955-56 surveys and may relate only to N-P-K mixtures, they indicate that the portion of the total P2O5 in water-soluble form increased from about 49% in 1880 to about 57% in 1925, and then decreased to 42.6%in 1935. The values were 46.9 and 43.4% in 1949-50 and 1955-56, respectively. The decreases between 1925 and 1950 followed development and utilization of ammoniating solutions, and those between 1949-50 and 1955-56 marked increased usage of such solutions in granulation and continuous ammoniation processes and the use of nitric acid in the production of available phosphates. Presumably the observed decrease between 1949-50 and 1955-56 was limited to some extent by introduction of sulfuric acid and (or) phosphoric acid into fertilizer formulas to aid granulation.

The available portion of the total P_2O_5 increased gradually from 75.5% in 1880 to 93.0% in 1949-50 and to 94.3% in 1955-56. This continued increase probably is due to the decrease in the portion of the P2O5 derived from organic materials, process improvements in the production of superphosphate, and the change in the official method for available phosphorus which in 1931 decreased the weight of the analytical sample from 2 grams to 1 gram and increased the period of digestion from 30 to 60 minutes (3). Between 1925 and 1935 the water-soluble portion of the available P2O5 decreased from approximately 64 to 46%, increased to 48.4%for N-P-K grades alone, and to 50.2%for all mixtures in 1949-50, and decreased to 43.2 and 45.8%, respectively, in 1955-56.

PART II. REACTION, PARTICLE SIZE, AND INERT MATTER CONTENTS

Analytical Methods

Moisture, acid-insoluble ash, and calcium carbonate equivalent of carbonate carbon contents, and the acidor non-acid-forming qualities of the samples were determined by duplicate analyses (2). The vacuum-desiccation procedure was used in determination of the free-moisture content and the dried residues therefrom were used in the determination of the acid-insoluble ash.

The glass-electrode procedure was used in determining the acid-base

balance required for calculation of the acid- or non-acid-forming quality. In most instances the fertilizer control officials supplied the nitrogen analysis needed in the calculation, but in a few cases where the nitrogen analyses were not available, the guaranteed nitrogen grade was used in the calculation. The uncertainty introduced by this substitution probably did not exceed 5 pounds of calcium carbonate equivalent per ton of mixture. The citrate-insoluble P_2O_5 values determined in connection with the phase

of the survey concerned with the different forms of phosphorus were used in the calculation.

Two parts of cooled, boiled, distilled water were used per part of fertilizer to determine the pH of the sample at 25° to 30° C. by the glass electrode procedure.

The particle-size distribution of samples received in the unground condition was determined with the use of 4-, 6-, 20-, and 28-mesh Tyler standard screen scale sieves. The nested assembly of sieves was shaken in a Rotap machine for a period of 3 minutes, after which the weight of material retained on each sieve and collected in the pan was determined to the nearest 0.1 gram.

Screen Analyses. As indicated in Table VII, 83 of the 103 superphosphate and 393 of the 491 mixed fertilizer samples were received in unground condition and subjected to the screen analysis described above. The data are summarized in this table to indicate the distribution of the samples in relation to the ± 20 -mesh and -28-mesh fractions.

As shown by both sections of the table, increases in the +20-mesh fractions are more or less regularly associated with corresponding decreases in the -28-mesh fractions with no distinct division between granular and nongranular materials. However, the samples may be conveniently classified into nongranular, semigranular, and granular materials by the broken lines in each section of the table. The nongranular classification then applies to products containing 0 to 40% +20-mesh material, semigranular to products containing

Table VII. Distribution of Superphosphates and Mixed Fertilizers in Relation to Screen Analyses

| +20-Mesh | | — 28-Mesh Portion, Range, % | | | | | | | | | | | | |
|-----------------------------------|--------------------|-----------------------------|-------|------------|------------|-------------|--------------------|--------------------|-------|--------|-----------------------------|--|--|--|
| Portion, Range, % | 0-10 | 11-20 | 21-30 | 31-40 | 41-50 | 51-60 | 61-70 | 71-80 | 81-90 | 91-100 | Totol | | | |
| 70 | | % of Total Samples | | | | | | | | | | | | |
| | | | | | 83 Superpl | nosphates | | | | | | | | |
| 0-10 11-20 21-30 31-40 | 1.2 | | | | | 7.2 | 1.2 25.3 4.8 | 9.6 3.6 | | 1.2 | 2.4 10.8 28.9 12.0 | | | |
| 41-50 51-60 | | 1.2 | | 1.2 7.2 | 6.0 | 2.4 | | | | | 10.8 7.2 | | | |
| 61-70 71-80 81-90 91-100 | 2.4 1.2 12.0 | 1.2 4.8 | 6.0 | | | | | | | | 7.2 7.2 1.2 12.0 | | | |
| Total | 16.9 | 7.2 | 6.0 | 8.4 | 6.0 | 9.6 | 31.3 | 13.3 | ••• | 1.2 | 100.0 | | | |
| | | | | 3 | 93 Mixed | Fertilizers | | | | | | | | |
| 0-10 11-20 21-30 31-40 | 0.5 | | | 0.3 | 2.3 | 3.1 10.7 | 2.0 36.9 0.8 | 0.5 17.3 3.8 | 2.3 | | 0,5 21.6 44.5 13.7 | | | |
| 41–50 51–60 | | | 0.3 | 2.0 1.5 | 3.6 | | | | | | 5.6 1.8 | | | |
| 61-70 71-80 81-90 91-100 | 0.3 1.0 4.6 | 0.8 2.5 1.0 | 2.0 | | • | | | | | | 2.8 2.8 2.0 4.6 | | | |
| Total | 6.4 | 4.3 | 2.3 | 3.8 | 5.9 | 13.7 | 39.7 | 21.6 | 2.3 | | 100.0 | | | |