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, %	010	11-20	21-30	31-40	41-50	51-60	61-70	71-80	81-90	91-100	Totol
70					~ %	of Total Sam	ples				
					83 Superp	hosphates					
0-10	1.2									1.2	2.4
11-20 21-30							1.2 25.3	9.6 3.6			$\frac{10.8}{28.9}$
31-40						7,2	4.8	5.0			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	$\begin{array}{c} 0.5\\ 17.3\\ 3.8\end{array}$	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
6170 71-80 81-90 91-100	0.3 1.0 4.6	0.8 2.5 1.0	2.0			•••••					1.8 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

Table VIII. Summary of Screen Analyses of Superphosphates and Mixed Fertilizers

					Pa	ortion Re	tained or Passed	l by Indi	coted Sieves,	%		
	Sa	mples	+4	Mesh	-4,+0	6 Mesh	-6, +20 /	Mesh	-20, +28	3 Mesh	-28 M	esh
ltem	No.	$\mathbf{\%}^{a}$	Range	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
			Nongr	anulai	Materials,	0-40%	+20 Mesh					
All superphosphates Superphosphate, 18–20% Superphosphate, 45–48% All mixtures	44 37 7 ^b 313 ^c	53.0 64.9 26.9 79.6	0-5.1 0-5.1 0-0.4 0-4.8	$0.4 \\ 0.5 \\ 0.1 \\ 0.2$	0-9.0 0-9.0 0-4.9 0-6.7	2.6 2.8 1.5 1.9	7.0-34.5 7.0-31.0 22.2-34.5 1.1-37.6	22.5 21.6 27.2 22.3	2.3-27.1 2.3-27.1 5.3-8.9 3.0-26.7	7.4 7.4 7.4 9.1	55.9-77.2 56.8-77.2 55.9-68.8 45.1-86.3	67.1 67.7 63.8 66.5
			Semigr	anular	Materials,	41-609	6 + 20 Mesh					
All superphosphates Superphosphate, 19–20% Superphosphate, 42–45% All mixtures	15 11 4 29	18.1 19.3 15.4 7.4	0-1.9 0-1.9 0-1.3	$ \begin{array}{c} 0.3 \\ 0.4 \\ 0.0 \\ 0.1 \end{array} $	0-7.4 0-7.4 0-8.8	2.7 3.6 0.0 2.8	34.1-55.8 34.1-55.8 42.5-48.5 35.5-55.9	46.4 46.5 46.1 44.7	5.9-34.6 5.9-11.7 7.1-34.6 6.4-19.3	10.9 9.0 16.2 12.0	19.1-51.6 32.6-51.6 19.1-45.7 30.8-50.3	39.7 40.4 37.7 40.4
			Gran	ular M	aterials, 61	-100%	+20 Mesh					
All superphosphates Superphosphate, 20% Superphosphate, 45-46% All mixtures	23 9 14 48	27.7 15.8 53.8 12.2	0-9.9 0-9.9 0-23.0	$ \begin{array}{c} 0.5 \\ 1.2 \\ 0.0 \\ 0.9 \end{array} $	$\begin{array}{r} 0-65.7\\ 3.8-65.7\\ 0-21.4\\ 0-23.6\end{array}$	6.6 13.7 2.0 6.4	$\begin{array}{c} 19.1 - 100.0 \\ 19.1 - 75.5 \\ 63.7 - 100.0 \\ 23.6 - 97.3 \end{array}$	78.2 60.5 89.6 74.5	$0-14.7 \\ 0.3-14.4 \\ 0-14.7 \\ 0-17.5$	4.8 6.7 3.6 6.9	0-27.2 5.0-27.2 0-25.4 0-27.5	9.9 18.0 4.8 11.3
^a Based on numbers of samp	les: all	superpl	hosphates	s, 83;	18–20% sup	perphos	ohates, 57; 42	2-48%	superphosp	hates, 2	6; mixed fer	tilizers,

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^b Not including one sample which analyzed 87.3% passing 20- and retained on 28-mesh sieves. ^c Not including three samples two of which analyzed 69.9 to 71.1% passing 20- and retained on 28-mesh sieves and the third 70.4% passing the 20-mesh sieve with 37.5% passing the 28-mesh sieve.

Table X. Distribution of Superphosphates and Mixed Fertilizers in Relation to pH

	% of Tota	I Samples
pH Range	103 super- phosphates	491 mixed fertilizers
2.0-2.4	30.0	0.4
2.5-2.9	66.0	3.1
3.0-3.4	3.9	10.6
3.5-3.9		28.1
4.0-4.4		25.9
4.5-4.9		18.9
5.0-5.4		8.1
5.5-5.9		2.9
6.0-6.4		1.2
6.5-6.9		0.6
7.0-7.4		0.2
Total	99.9	100.0

Table XI. Distribution of Superphosphates and Mixed Fertilizers in Relation to Moisture Content

10	Kelüllön	to motsible	Comen
	Moisture	% of Totol	Samples
	Content, Range, %	103 super- phosphates	491 mixed fertilizers
	$\begin{array}{c} 0-0.50\\ 0.51-1.00\\ 1.01-1.50\\ 2.01-2.50\\ 2.01-2.50\\ 2.51-3.00\\ 3.01-3.50\\ 3.51-4.00\\ 4.01-4.50\\ 4.51-5.00\\ 5.01-5.50\\ 5.51-6.00\\ 6.01-6.50\\ \end{array}$	20.4 32.0 25.2 7.8 6.8 3.9 1.9 1.0 	13.423.420.215.19.65.93.73.92.61.40.40.20.2
	Total	100.0	100.0

41 to 60% +20-mesh material, and granular to products containing 61%or more +20-mesh material.

A summary of the screen analysis data grouped according to the above classification is given in Table VIII.

The proportion of mixed fertilizers marketed in granular form in 1955-56 (12.2%) compares well with the 8.8%of all mixed fertilizer reported consumed in granular form in the continental United States by Scholl, Wallace, and Fox (8). On the average typical nongranular products contained about onefourth +20-mesh material and two-thirds -28-mesh. Semigranular products averaged about 50% of -20-mesh and 40% of -28-mesh, whereas granular products averaged 75 to 90% +20-mesh material.

Analytical Data. A summary of the analytical data in relation to the different classifications of superphosphates and

mixtures is given in Table IX. This table also indicates for each region the average grade of the samples and the numbers of samples, manufacturers, and states involved.

In general, the superphosphates were more acid in reaction than the several groups of mixed fertilizers. The concentrated superphosphates were the most acid, with a median pH value of 2.3 in contrast to 2.6 for normal superphosphates, 3.0 for P-K, 3.9 for N-P, 4.1 for N-P-K, and 6.4 for N-K grades. The pH values for superphosphates ranged from 2.0 to 3.1, for $N-\hat{P}$ and P-Kmixtures from 2.4 to 4.5, for N-K mixtures from 4.8 to 7.1, and for N-P-K mixtures from 2.8 to 6.9.

The moisture content of the superphosphates ranged from 0.2 to 4.7 and averaged 1.2% and that of the mixed fertilizers from 0.1 to 6.2% and averaged 1.6%. These values are believed, in general, to be somewhat lower than those prevailing at the time the samples were drawn owing to unavoidable changes during storage and sample preparation,

The distributions of the superphosphates and mixed fertilizers in relation to pH and to moisture content are shown in Tables X and XI, respectively.

Except for the N-P and P-K grades, the mixed fertilizers contained more acid-insoluble ash and except for the N-P grades more carbonate carbon than the superphosphates. In 1954, 97.6% of the P_2O_5 content of mixed fertilizers was supplied by superphosphates (1). On the average, therefore, and assuming that the P2O5 is derived entirely from superphosphates, a ton of mixed fertilizer in 1955-56 appears to have contained about 150 pounds of acidinsoluble ash in excess of that contributed by the superphosphate, and also about 95 pounds of calcium carbonate equivalent. These figures compare with 150 and 100 pounds, respectively, reported in the 1949-50 survey. Nearly one eighth of the average mixed fertilizer in both surveys, therefore, consisted of materials not primarily useful as sources of the major plant-nutrient elements-nitrogen, phosphorus, and potassium.

The N-P grades were second highest in average plant-nutrient content, 31.7%, contained the least acid-insoluble ash and carbonate carbon, and were highest in acid-forming quality, 923 pounds CaCO3 equivalent per ton. The N-K grades were lowest in average plantnutrient content, 23.6%, highest in acid-insoluble ash and carbonate carbon, and second highest in acid-forming quality, 491 pounds per ton. The P-K group was the highest in plant-nutrient

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Relation
2.
Fertilizers
and Mixed
vperphosphates a
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ē
Distributions
Table IX.

										Acid-Insoluble	uble	Ŭ	aCo ₃ Equiv	CaCo ₃ Equivalent, lb./Ton Acid- or Non-Acid-	-Acid-
		No. of	No. of	No. of		Hq		Moisture,	%	Ash, Ib. /Ton		Carbonate Carbon	Carbon	Forming Quality ^a	ulity"
	Region Fertilizer Classification	Samples	States	Mfrs.	Average Grade, %	Range	Median	Range	Mean	Range	Mean	Range	Mean	Range	Mean
ž	New England Superphos., 18-20%	11	3	6		2.4 - 3.1		0.4 - 4.7	1.7	53-214	102	0^{-33}	ъ.	4B-84	37
	Superphos., 46%	14	- 7	1 4	0-46.0-0 5 21 10 50 11 75	о с : · ·	2.3 7 Y		1.0	77, 77	41 173	0-333		141R_673	66 096
	All mixtures P–K grades	7 7	n <>	<u>,</u> 2	0.14.50-22.00	2.9-3.1		2.6-3.9	3.2 2.2	23 -165	94 94	64-0	> (1	141B-26	58B
	N-P-K	14	ر ي ا	12	6.64 - 9.93 - 10.29	3.8-5.2			1.9	28-477	184	0^{-333}		55673	316
Μ	Middle Atlantic Superphos., $18-20\%$		9	14		2.4–28	2.6	ς.	0.8	50-186	92	0-41	9	147B-59	18
	All mixtures	29	ഗര	26	5.61-10.81-9.14	ထုံ ၀	6. c	0.3 - 3.7	0.0	33-540	206	2-415 7 26	97 15	212B-8/5 106B-24B	197 67B
	F-n grades N-P-K grades	56	ر ي ار	26^{4}	5.91 - 10.43 - 8.66	3.3-5.5	3.9	• •	1.0	33-540	214	2-415	102	212B-875	211
Sc	South Atlantic Superphos., $18-20\%$	11	4	6		2.52.9	•	0.4 - 3.3	1.6	57-208	105	1 - 10	4,	42B-34	900
	Superphos., 46%	1 1	, - ч	1	0-46.00-0	2 0 7 1	7.7 7.7	9 C	2. c 4. f	31070	29 210	3-603	114	4728-1486	82 44
	All mixtures N–K grades	0 2 - C	04	6 4 10	4.03-9.16-6.43 11.60-0-12.00	4.8-7.1		0.2 - 1.7	0.7	22-1079	263		173	144B-1486	491
	P-K grades	1 7 2 2 2 2	ωu	5.5	0-14.80-15.60	2.9 - 3.4	3.2	•	2.0	58-150 3-884	99 378	3-74 3-603	115 115	129B-12B 472B-958	73B 34
,	N-r-h graucs		، ر	5 ;					1 -		070				
2 1	East North Central Superphos., 20% All mixtures	111	ю г.	10 31	0-19.83-0 4.28-13.22-14.16	2.4 - 3.1 - 5.6	3.8 3.8	0.5 - 2.3 0.2 - 4.0	1.2	48-15/ 21-445	81 106	$1-19 \\ 0-335$	0 48 0	961B-1229	14 208
	P-K grades	8 01	ςΩĽ	9 9 7	0-17.50-21.25	2.6-3.5	3.1 8	0.4-1.7	1.1	21-80 21-45	111 111	0-221 1-335	39 49	481B-175 142B-1220	10B 231
141	Meet North Central Sumershoe 18-	9) e	9	0-19 70-0	2 4-2 6	2.0 2 6	9		44-180	82	4 1		23B-72	26
	20%	•	n	þ		•	2				1	-	2		1
	Superphos., 42 -48%	13	5	11	0-45.20-0	2.1-2.5	2.3	0.2 - 2.6	1.2	25-85	67	0-12	с ș	50B-102	38
	All mixtures	47	ഹ .	58 78	7.04 - 16.95 - 9.36	4. 7.4.	3.9	0.1-5.2	1.2 8.7	2-574	81 77	0-607 3-0	39 5	407B-1824 335 -1072	458 603
	N-F grades P-K grades	2 4	ب 4	4 ر		2.4 - 3.0	2.7	0.3 - 1.2	0.6	41-455	150	2-9	ο ro	195 B -24 B	121B
	N-P-K grades	34	5	3	7.0914.9111.29	2.9 - 5.9	4.1	0.1 - 4.6	1.1	2-574	85	0-607	51	407B-1824	464
Ę	East South Central Superphos., 20%		÷.	L e		$\dot{\dot{\gamma}}$	2.5	0.3 - 3.3	1.2	50-100	73	2 -6	1 09		43
	Superphos., 45–49% All mixtures	7 29	- 7	7 80	0-4/.00-0 4 26-10 13-8 30	୍ଚ	7.4 7.7	$0.4^{-1.2}$ 0 5-4.9	0.0 - 1	28-503	c/ 171	2-12	212	747B-515	91 8B
	P-K grades	14	+ 4	4	0-14.00-14.00	.9-3.	3.1	1.4-2.3	1.9	40-135	82	2-14	9	518-7	21B
	N-P-K grades	58	4	27	4.55 - 9.86 - 8.00	. 5–6.	4.5		2.1	28-503	177	4-792	226	747B-515	7 B
	West South Central Superphos., 20%	, c 1 c		.	0-20.00-0		2.4		0.5	72 04	62 6		4 п		14 13R
	Superphos., 45–48% All mixtures	0 1 14 0	- ന	12 0	6.07-11.29-9.36	3.1-5.9		$0.2^{-0.7}$	1.0	73-569	196	2-579	132	399 B -930	250
	N-P grades	- 5	- ~	- 5	10.00-20.00-0 5 77 10 62 10 08		3.5		0.6	73.560	45 208	2-570	5 147	300R-030	793 208
	IN-T-IN graues	<u> </u>	י ר	: "	0.10.50.0	с ч		4 2 2 2		87_148	100	1_10	1 1	14 -51	31
	Mountain Superphos., 19–20% Superphos., 42-46%	4 ∞	ن ہ	04	0-19.30-0 0-44.90-0	2.2-2.6	2.4 4.0	$\dot{\gamma}$	1.2	43-81	62	1-14	, 4	30B-74	42
	All mixtures N - D mades	01 م	4 %	ഗഗ	9.10-16.90-2.50 10.60-21.00-0	<u>4</u> 4		0.4-4.0 0 4-4 0	2.0 0.5	20-585 20-76	189 42	2^{-16}	- 4	46 -1719 435 -1719	809 1037
	N-P-K grades	л ro	ر ي ر	4	7.60-12.80-5.00	2.8-4.9	4.2		1.4	37-585	336	3-16	. 6	46 -1134	581
ڪ FEI	Pacific Superphos., 19%		-	1 ,	0-19.00-0		•	0 1 1 2	0.9	71 221	110 116		с, т		53 1201
В.	All mixturcs N_P oracles	4 C		0 C	12.12-0-12-0-12.12 16.50-8.50-0	4-0 	0 00 0 00		0.0	21-30	26	2 - 7 	+ «	1695 -1786	1740
19	N-P-K grades	10		1 0	9.00-9.00-4.50	3.3-4.5		0.7 - 1.3	1.0	82-331	207	3^{-6}_{-6}	9	779 -904	842
	United States Superphos., 18–20%	75 28	26 12	41 17	0-19.70-0	2.3-3.1	2.6 7	0.3-4.7	1.2	44-214 25-85	92 66	0-41	ഗഗ	147B-84 89B-102	24 35
	All mixtures	491	35	160	5.26-11.42-9.91	4-7.	4.1	မှ	1.6	2-1079	203	0-792	98	747B-1824	171
0	N-P grades N. K mindee	17	84	14 ۲	11.00-20.70-0	2.6-4.5 4 8-7 1	3.9 6 4		1.0 4.0	20-76 22-1079	38 263	2 -9 6-360	173 4	335 -1786 144B - 1486	923 491
	P-K grades	26	16	. <u>18</u>	0-16.70-18.50	2.4-3.5	3.0	0.3 - 3.9	1.4	21-455	84	0-221	19	481B-175	78B
	1	443	35	146	5.28 - 10.88 - 9.76	2.8-6.9	4.1	0.1 - 6.2	1.6	2-884	216	0-792	105	747 B -1824	154
	^a B. Non-acid-forming.														

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content, 35.2%, next to the lowest in acid-insoluble ash and carbonate carbon, and the only group which was non-acid-forming, 78 pounds per ton.

The N-P-K grades were next to the lowest in plant-nutrient content, 25.92%, next to the highest in acid-insoluble ash and carbonate carbon, and the lowest acid-forming group, 154 pounds per ton.

The data on acid-insoluble ash, carbonate carbon, and acid- or nonacid-forming quality are summarized in Table XII in relation to the principal grades of mixed fertilizers and superphosphates. Wide variations in ash and carbonate carbon contents, and in net acid-base balance were noted for all grades listed. In comparison with the superphosphates the mixtures, with the exception of the 0-20-20, 4-16-16, 5-20-20, and 10-10-10 grades, contained considerably greater quantities either of acid-insoluble ash, carbonate carbon, or both.

Acid-Insoluble Ash and Calcium Carbonate Equivalent of Carbonate Carbon. Table XIII shows the distribution of the mixed fertilizer samples in relation to acid-insoluble ash content, sum of the ash content and CaCO₃ equivalent of the carbonate carbon and the interrelation of these quantities. More than 45% of the samples (45.4%). 223 samples) contained less than 100 pounds of acid-insoluble ash per ton, and about 57% of these (127 samples) exhibited sums of ash content and CaCO₃ equivalent of carbonate carbon of less than 100 pounds. Nearly 30% (28.6%, 64 samples) exhibited sums of 101 to 400 pounds and 14% (14.3%, 32 samples) sums between 401 and 700 pounds. More than three eighths of the samples (38.1%, 187 samples)contained 101 to 400 pounds of ash and of these more than one fourth (26.7%, 50 samples) contained 401 to 700 pounds of ash plus calcium carbonate equivalent of carbonate carbon. Approximately 16% of the samples (16.4%, 81 samples) contained more than 401 pounds of ash and of these at least 38 also contained appreciable amounts of carbonate carbon.

Carbonate Carbon and Acid-Forming Quality. Distribution of the samples in relation to the CaCO₃ equivalent of the carbonate carbon content, the CaCO₃ equivalent of the acid-forming quality or the acid-base balance, and the interrelation of these quantities is given in Table XIV. One hundred and fifty-eight (32.2%) of the samples

 Table XII.
 Summary of Acid-Insoluble Ash and Calcium Carbonate Equivalent Contents, and Acid- or Non-Acid

 Forming Quality of Superphosphates and Principal Grades of Mixed Fertilizers

							CaCC	3 Equivalent, Lb./Ton	
	No. of	No. of	No. of	Acid-Insoluble	Ash, Lb./Ton	Carbonate	e Carbon	Acid- or Non-Acid-Fo	orming Quality ^a
Grade, %	Samples	States	Mfrs.	Range	Mean	Range	Mean	Range	Mean
				Super	phosphates				
P2O5									
18 to 20	75	27	41	44-214	92	0-41	5	147B-84	24
42 to 49	28	12	17	25-85	66	0-14	5	89B-102	35
Total	103	30	54	25-214	85	0-41	5	147B-102	27
				Mixed	d Fertilizers				
N-P2O5-K2O									
3-12-12	54	12	31	31-416	159	1-607	80	407B-1824	102
5-10-10	43	14	26	34-526	219	2-390	88	212B-499	187
3-9-6	27	6	18	58-535	299	43-792	224	747B-153	127B
4-16-16	23	8	16	31-157	57	3-105	16	39 - 396	201
5-10-5	21	13	15	35-596	277	2-579	185	399B-369	93
10-10-10	21	12	15	21-166	46	2-51	17	377 -1229	712
3-9-9	19	5	15	51-525	261	57-535	174	412B-4 0	105B
4-10-6	16		13	61-618	402	7-451	133	378B-235	13B
4-10-7	16	3 3	13	32-410	207	96-539	283	465B-26	148B
4-8-8	14	3	13	36-808	531	3-603	105	472B260	27
4-12-12	14	4	13	56-280	156	4-188	55	87 B -256	99
2-12-12	13	4	12	64-377	180	4–180	68	211B-95	31B
0-20-20	11	9	9	41–456	91	057	12	195B-175	84B
6-12-12	10	4	4	51-188	104	3-61	21	147 -515	345
4-8-6	10	2	10	606-844	678	5-212	63	178 B -229	73
5-20-20	10	7	9	22-58	32	2-61	13	183 -424	270
16 grades	322	28	113	21-844	217	0-792	102	747B-1824	107
74 other grades	169	33	87	2-1079	177	0-533	89	481B-1786	295
Total	491	35	160	2-1079	203	0-792	98	747B-1824	171
^a B. Non-acid-	forming.								

Table XIII. Distribution of Mixed Fertilizers in Relation to Content of Acid-Insoluble Ash, and Sum of Ash Content and Calcium Carbonate Equivalent of Carbonate Carbon

Acid Insoluble			Acid-Insol	luble Ash plus	CaCO ₃ Equi	valent of Car	bonate Carb	oon, Range,	Lb./Ton		
Ash, Range, Lb./Ton	0-100	101-200	201-300	301-400	401-500	501-600	601-700	701-800	801-900	1001-1100	Total
				%	of Total San	nples					
0-100	25.9	6.3	5.1	1.6	3.7	2.2	0.6				45.4
101-200		5.7	4.3	2.4	1.6	0.2	0.2		0.4		14.9
201-300			5.7	3.3	1.4	0.8					11.2
301-400				4.1	4.7	2.6	0.6				12.0
401-500					2.4	3.5	0.6				6.5
501-600						3.1	2.0	0.4			5.5
601-700							0.6	0.8			1.4
701-800								1.4	0.4		1.8
801-900									1.0		1.0
1001-1100										0.2	0.2
Total	25.9	12.0	15.1	11.4	13.8	12.4	4.7	2.6	1.8	0.2	99.9

were non-acid-forming compared with 167 (34.0%) which contained more than 100 pounds of CaCO3 equivalent of carbonate carbon per ton and 76 (15.5%) which contained in excess of 200 pounds of carbonate equivalent. Of the 167 samples containing more than 100 pounds of CaCO3 equivalent of carbonate carbon per ton 52 (31.1%) were acid-forming and 115 (68.9%) non-acid-forming. Approximately 44% (44.4) or 218 samples were acid-forming in the range of 0 to 300 pounds of CaCO3 equivalent per ton, compared with 144 (29.3%) which were non-acidforming in the same range. Fourteen of the mixtures (2.8%) were non-acidforming in excess of 300 pounds of CaCO₃ equivalent per ton and 23.4% (115 samples) were acid-forming in this range.

Phosphorus, Ash, and Carbonate Carbon Contents. Inasmuch as the superphosphates are the principal phosphorus sources used in formulating mixtures (1) and also the principal ingredients normally carrying an appreciable acid-insoluble ash content, a comparison of the ash content of mixtures and of superphosphates in relation to their phosphorus content provides an approximate measure of the inert material that was added. Such a comparison is presented in Table XV for mixtures collected in two or more grades for each of 17 different plant-nutrient ratios. Similar comparative data also are tabulated for CaCO3 equivalent of carbonate carbon and acid- and nonacid-forming quality. Although these latter quantities are more closely related to nitrogen content than to the phosphorus in the mixtures, the values for grades having the same plant-nutrient

CoCO₃ Equivalent

Carbon

ratio are in approximately the same proportion in either case. Inspection of the table indicates that the lower analysis mixtures contained from 1.5 to 14 times as much acid-insoluble ash as would normally be associated with their phosphorus content, assuming that the phosphorus is derived entirely from superphosphates. Seven of the principal grades-3-9-6, 3-9-9, 3-12-12, 4-8-8, 4-12-12, 5-10-5, and 5-10-10contained 2.8 to 14 times as much ash as the equivalent superphosphate. The data indicate that it would be possible in many cases to formulate higher analysis grades of the same plantnutrient ratio without the use of concentrated superphosphates, and that such a practice would appreciably reduce the necessity for the addition of makeweight material. In other cases this can be and is being done economically by partial replacement of normal superphosphate with triple superphosphate or other high analysis phosphates. The data also indicate that in general the acid-forming quality of the mixtures increases and the CaCO3 equivalent of the carbonate carbon content decreases as formulation of an individual plant nutrient ratio proceeds to the higher analysis grades.

Economic Significance

As indicated in Table IX, the average mixed fertilizer marketed in 1955-56 contained 203 pounds of acid-insoluble ash (an increase of 3.6% over 1949-50) and 98 pounds of CaCO₃ equivalent of carbonate carbon per ton (a decrease of 10.1% compared to 1949-50). Similarly, the average normal superphosphate

Table XIV. Distribution of Mixed Fertilizers in Relation to Content of Calcium Carbonate Equivalent of Carbonate Carbon and Acid- or Non-Acid-Forming Quality^a

contained 92 pounds of ash and 5 pounds of carbonates per ton. The corresponding figures for concentrated superphosphate are 66 and 5 pounds, respectively. Scholl, Wallace, Fox, and Crammatte (9) reported that 14,529,159 tons of mixtures containing 1,880,409 tons of total P2O5 were marketed in continental United States in the year ending June 30, 1956. Based on the figure for acid-insoluble ash content, the mixtures marketed in 1955-56 contained 1,474,710 tons of insoluble ash, of which 404,290 tons would be associated with the normal superphosphate equivalent of the mixtures or 131,630 tons with the concentrated superphosphate equivalent. Inasmuch as both normal and concentrated superphosphates are used in the formulation of many mixed fertilizers, the acid-insoluble ash content of the mixtures in excess of that contributed by the superphosphate components lies between 1,070,420 and 1,343,080 tons. Assuming, however, that the usage of normal and concentrated superphosphates in mixed fertilizer formulation is approximately proportional to the available P2O5 contents of their productions in this period (1,526,115 and 754,694 tons of P_2O_5 , respectively) (11), the estimate for acid-insoluble ash associated with the superphosphate content of the mixed fertilizers becomes 314,070 tons. Thus, a net of 1,160,640 tons (1,474,710 -314,070) of ash are estimated as being added in the make-weight and neutralizing materials used in preparing the mixtures.

Similarly, the marketed mixtures are estimated to contain 711,930 tons of CaCO₃ equivalent of carbonate carbon, of which 19,180 tons were associated with superphosphates. Thus, it is esti-

of Carbonate Acid- or Non-Acid-Forming Quality, Range, Lb. CoCO₃ Equivalent/Ton

Range,					401-	<u>,,</u> g.,	601-		801-		1001-	Tot	al
Lb./Ton	0-100	101-200	201-300	301-400	500	501-600	700	701-800	900	901-1000	1900	Subtotal	Total
				%	6 of Tota	al Samples in	Indicate	ed Ranges					
0-100 A	10.6	13.6	11.6	7.1	4.1	1.0	1.2	1.8	1.6	1.4	3.1	57.2	66.0
В	6.5	2.0	0.2									8.8	
101–200 A	3.3	1.6	0.6	1.0	0.2					0.2		6.9	18.5
В	8.4	3.1	0,2									11.6	
201-300 A	2.0	0.6										2.6	7.3
В	1.6	2.9			0.2							4.7	
301-400 A		0.2			0.2	0.2						0.6	2.9
В	0,8	0.6	0.8									2.2	
401–500 A	0.2			0.2								0.4	3.1
В		1.0	1.2	0.4								2.6	
501–600 A													1.4
В				0.8	0.6							1.4	
601–800 A													0.8
В					0.4	0.2		0.2				0.8	
Subtotal A	16.1	16.1	12.2	8.4	4.5	1.2	1.2	1.8	1.6	1.6	3.1	67.8	100.0
В	17.3	9.6	2.4	1.2	1.2	0.2		0.2		1.0	0.1	32.2	
Total	33.4	25.7	$\frac{14.7}{14.7}$	9.6	5.7	$\frac{3.2}{1.4}$	1.2	$\frac{3.2}{2.0}$	1.6	1.6	3.1	100.0	
					2.,				1.0	1.0	5.1	100.0	
^a A, acid-	forming;	B, non-aci	d-forming	•									

							CaC	O ₃ Equival	ent, Lb./Unit Total	P2O5
Plant-Nutrient	Grade.	No. of	No. of	No. of	Acid-Insolub Lb./Unit To		Carbonate	Carbon	Acid- or No Forming Qu	
Ratio, N−P2O5−K2O	%	Samples	States	Mfrs.	Range	Mean	Range	Mean	Range	Mean
				5	Superphosphate	5				
0-1-0	18-20 42-49 Total	75 28 103	26 12 30	41 17 54	2.0-11.7 0.5-1.9 0.5-11.7	4.3 1.4 3.5	0-2.0 0-0.3 0-2.0	0.2 0.1 0.2	6.8B-4.5 1.9B-2.1 6.8B-4.5	$1.1 \\ 0.7 \\ 1.0$
					N-P Mixtures					
1-2-0	10-20-0 12-24-0	6 1	5 1	5 1	1.2-3.1	2.2 1.1	0.2–0.3	$\begin{array}{c} 0.2\\ 0.2\end{array}$	17.7 -54.2	35.3 30.9
1-4-0	6-24-0 8-32-0	1 3	1 3	1 3	0.7-1.2	2.0 0.9	0.1-0.3	$\begin{array}{c} 0.3\\ 0.2 \end{array}$	13.4 -20.0	13.8 16.1
					P-K Mixtures					
0-1-1	0-14-14 0-20-20	9 11	8 9	8 9	2.7-11.4 1.8-22.2	6.3 4.4	0-1.0 0-2.5	0.4 0.6	4.6B-1.8 9.5B-7.5	1.9B 4.2B
				1	N-P-K Mixture	s				
1-1-1	5-5-5 6-6-6 7-7-7 8-8-8 10-10-10 12-12-12 13-13-13 14-14-14	1 3 1 6 21 7 1 1	1 1 5 12 7 1	1 3 1 5 15 6 1 1	16.5-24.7 3.6-12.8 1.9-16.5 0.8-4.0	45.4 20.7 6.4 7.5 4.3 2.3 0.4 0.2	1.7-2.3 0.3-29.8 0.2-5.0 0.1-2.5	$\begin{array}{r} 4.5 \\ 1.9 \\ 38.9 \\ 16.5 \\ 1.6 \\ 0.7 \\ 0.3 \\ 0.0 \end{array}$	28.1 -39.5 5.1B-76.0 29.1 -108.1 23.3 -125.1	2.1B 34.0 18.8 42.6 64.9 71.7 102.5 98.9
1-2-1	5-10-5 6-12-6 10-20-10	21 1 2	13 1 2	15 1 2	3.1-55.8 2.1-2.3	25.4 11.4 2.2	0.2-55.6 0.3-1.9	$\begin{array}{c}17.1\\0.4\\1.1\end{array}$	38.3B34.5 17.1 -34.0	8.4 30.4 25.6
1-2-2	4-8-8 5-10-10 6-12-12 8-16-16 10-20-20	14 43 10 4 1	3 14 4 4 1	13 26 5 4 1	4.4-97.1 3.3-53.7 4.1-14.3 1.4-2.4	$61.6 \\ 20.2 \\ 8.1 \\ 1.8 \\ 0.2$	0.3-76.2 0.2-35.3 0.2-4.9 0.4-10.6	12.6 8.0 1.7 3.4 0.2	59.6B-30.6 19.2B-49.0 12.0 -43.5 21.4 -33.1	2.6 17.3 27.4 27.1 47.0
1-2-3	4-8-12 5-10-15	1 3	1 2	1 3	4.3-8.7	42.2 7.1	0.4-14.8	21.1 9.5	23.8 -30.9	4.6B 28.4
1-3-1	4-12-4 8-24-8	3 3	2 1	3 3	2.4-46.2 1.3-2.3	29.6 2.0	0.4-31.3 0.2-0.7	10.7 0.4	9.5B-25.5 12.8 -20.1	11.2 16.8
1-3-2	3-9-6 4-12-8	27 6	5 5	9 5	6.4-56.2 4.3-27.1	29.7 12.7	4.2-90.4 0.3-12.5	23.0 3.3	83.5B-15.0 0.8B-14.9	13.5B 9.7
1-3-3	3-9-9 4-12-12	19 14	5 4	16 13	5.0-54.9 4.1-23.1	26.5 12.4	5.7-53.9 0. 3- 13.9	17.8 4.3	41.5B-3.9 6.6B-20.3	10.8B 7.8
1-4-2	3-12-6 5-20-10 6-24-12	8 1 1	3 1 1	7 1 1	6.3–41.4 	19.2 3.4 1.4	0.2-19.8	9.9 0.1 0.0	13.2B–11.0 	0.8 16.2 9.9
1-4-4	3-12-12 4-16-16 5-20-20	54 23 10	12 8 7	32 16 9	2.2-33.4 1.9-11.0 1.0-2.7	12.1 3.5 1.5	0.1-41.6 0.2-6.0 0.1-3.2	6.0 1.0 0.7	27.9B-140.8 2.4 -22.6 8.7 -20.0	7.7 12.0 13.1
1-6-3	2-12-6 3-18-9 4-24-12	2 2 1	1 2 1	2 2 1	19.8–24.0 3.6–4.6	21.9 4.1 2.1	0.5-0.6 0.4-5.3	0.5 2.9 0.2	3.6 -9.6 0.2 -5.4	6.6 2.8 3.5
2-2-1	8-8-4 10-10-5	1 1	1 1	1 1		42.8 7.9		0.4 0.8		100.9 86.9
2-3-3	6-9-9 8-12-12	1 1	1 1	1 1		30.8 2.8		1.8 0.0		29.4 30.2
2-3-4	6-9-12 8-12-16	2 1	1 1	1 1	9.6-18.8	14.2 2.2		8.6 0.7	36.1 -40.0	38.0 48.6
• B. Non-acio	l-forming.							<u></u>		

Table XV. Comparison of Acid-Insoluble Ash and Calcium Carbonate Equivalent of Carbonate Carbon Contents, and Acid- or Non-Acid-Forming Quality of Single and Multiple Strength Grades of Superphosphates and Mixed Fertilizers

mated that 692,750 tons of CaCO₃ equivalent also were added during mixing operations. These estimates of 1,160,640 tons of acid-insoluble ash and 692,750 tons of CaCO₃ equivalent appear to be of the right order of magnitude. In 1956, Stanfield (10) estimated that

operating costs in solid mixed fertilizer plants ranged from \$4.63 per ton of product for a plant with an annual sales volume of 40,000 tons to \$17.20 for a 2500 ton plant. Scholl (6) reported 1223 mixing plants in the United States in the 1951–52 fertilizer season with a total rated annual production capacity of 27,597,700 tons. Assuming the same number of plants operative in 1955–56 the average annual production of each plant was 14,529,159/1223 or 11,880 tons. Based on Stanfield's estimates, the operating costs for this average plant

would be \$9.16 per ton of product. With bags and bagging at \$4.00 per ton and handling and transportation also at \$4.00 per ton, the manufacturing and distribution cost of mixed fertilizer from the average-sized plant in 1955-56 appears to have been \$17.16 in excess of the value of the primary plant nutrients. Using a figure of \$17.00, the cost to the consumer of the acid-insoluble ash added to mixed fertilizers in 1955-56 amounted to \$19,730,880. It is generally recognized that incorporation of liming material partially or completely to offset the acid-forming character of mixed fertilizers serves a useful purpose in some parts of the country, notably the South and Southeast. Assigning a value of \$3.50 per ton of CaCO₃ equivalent for this purpose, the net manufacturing and distribution cost of the 692,750 tons of CaCO₃ equivalent of carbonate carbon added to the mixtures amounted to \$9,352,125 (692,750 \times \$13.50). The total cost to the consumer, therefore, for the 1,853,390 tons of acid-insoluble ash and CaCO3 equivalent of carbonate carbon in excess of any plant-nutrient value amounted to \$29,083,005, or \$2.00 per ton of mixed fertilizer (an increase of \$0.17 per ton or 9.3% over 1949-50). The effect of omitting concentrated superphosphate from consideration as an ingredient of the mixtures would be to reduce the estimate for added acid-insoluble ash by 90,200 tons and the cost to the consumer from \$2.00 to \$1.90 per ton.

It appears that the unit cost of primary plant nutrients in mixed fertilizer can be substantially reduced, if the consumer limits his purchases to those grades which can be manufactured and distributed economically without excessive inclusion of either limestone or inert materials.

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Literature Cited

- (1) Adams, J. R., Scholl, W., Assoc. Am. Fertilizer Control Officials, Offic. Publ. 12, 63-74 (1958).
- (2) Assoc. Official Agr. Chemists, Wash-

- ington 4, D. C., "Official Methods of Analysis," 8th ed., 1955.
 (3) Brackett, R. M., Hanson, H. H., Kraybill, H. R., J. Assoc. Offic. Agr. Chemists 15(1), 38-47 (1932).
 (4) Clark K. C. Codder, V. L. Pletini, M. S. M. S.
- (4) Clark, K. G., Gaddy, V. L., Blair, A. E., Lundstrom, F. O., Farm Chem. **115**(6), 21, 23–6 (1952).
- (5) Clark, K. G., Hoffman, W. M., Ibid., 115(5), 17-20, 21, 23 (1952).
- (6) Scholl, Walter, Natl. Fertilizer Rev. **29**(2), 10-15 (1954). (7) Scholl, Walter, Wallace, H. M.,
- Fox, E. I., Agr. Chem. 10(6), 67-70D (1955)
- (8) Scholl, W., Wallace, H. M., Fox, E. I., J. Agr. Food Chem. 5, 20-7 (1957)
- (9) Scholl, W., Wallace, H. M., Fox, E. I., Crammatte, F. B., Com. Fertilizer **95,** 23-32 (1957).
- (10) Stanfield, Z. A., "Economic and Technical Analysis of Fertilizer Innovations and Resource Use," Chap. 7, Iowa State College Press, Ames, Iowa, 1957.
- (11) U. S. Department of Commerce, Bureau of the Census, "Facts for Industry, Superphosphate and Other Phosphatic Fertilizers, Summary for 1956," 1957.

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PHOSPHORUS AVAILABILITY

Crop Response to Ammoniated Superand Dicalcium Phosphate, phosphates as Affected by Granule Size, Water Solubility, and Time of Reaction with Soil

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Crop response to phosphorus in a series of nonammoniated and ammoniated ordinary and concentrated superphosphates and dicalcium phosphate was determined in greenhouse experiments. Heavy ammoniation decreased the water solubility of phosphorus in ordinary superphosphate from 70 to 14% and in concentrated superphosphate from 89 to 57%, chiefly because of conversion to dicalcium and more basic phosphates. With band application, yields of dry matter and of phosphorus with the ammoniated superphosphates were closely related to the amount of water-soluble phosphorus applied; but other than for dicalcium phosphate, granule size was of little importance. With phosphates mixed throughout the soil, both water solubility and granule size of the phosphates greatly influenced yields on most soils. Response decreased with increasing time of reaction (3 and 6 months) of the superphosphates with soil prior to cropping. Decrease in response with time was much less with granular than with fine superphosphates. Liming acid Hartsells fine sandy loam had variable effects on crop response to phosphates.