mately neutral solution (pH about 6.6). The ammoniated superphosphoric acid (11–33–0) may be added to water without danger of hydrolysis, whereas superphosphoric acid cannot. Adding sequestrant after ammoniation of the wet-process acid is feasible, but somewhat less effective than adding it during or before ammoniation.

Liquid fertilizers of other $N:P_2O_5:K_2O$ ratios may be made from sequestered 8–24–0 solution by adding urea, nitrogen solutions, or potash salts. These supplemental materials may be added simultaneously to the reaction vessel during the ammoniation process. For commercial plants that are not equipped with heat exchangers, the simultaneous addition of the ingredients is desirable in the production of a three-component liquid, since the negative heat of solution of potassium chloride will help keep temperature down during ammoniation.

In any of the recommended procedures described above, it is advisable, if practical, to maintain the liquid in the reaction vessel below 190° F. At temperatures above 190° F., the amount of vapor from the reaction vessel becomes appreciable, and the water must be added back to the product at the end of the test or the calculated loss added in excess before or during ammoniation; however, reaction temperatures as high as 215° F. had no detrimental effect on the salting-out properties of the products.

Studies of the use of wet-process acid in the production of liquid fertilizers are continuing. Promising results are being obtained by use of special ammoniating techniques. Interesting results have been obtained also with wet-process phosphoric acid that has been concentrated to about 70% of P_2O_5 content. A process for concentrating wet acid is being studied.

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Literature Cited

(1) Durgin, C. B., Lum, J. H., Malowan, J. E., *Trans. Am. Inst. Chem. Engrs.* **33,** 643–68 (1937).
(2) Phillips, A. B., Young, R. D., Heil, F. G., Norton, M. M., Fertilizer and Soil Chemistry Division, 134th Meeting, ACS, Chicago, Ill., September 1958.
(3) Slack, A. V., J. AGR. FOOD CHEM. **3,** 568–74 (1955).
(4) Striplin, M. M., Jr., McKnight, David, Megar, G. H., *Ibid.*, **6,** 298–303 (1958).
(5) Striplin, M. M., Jr., Stinson, J. M., Wilbanks, J. A., *Ibid.*, **7,** 623–8 (1959).

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FERTILIZER TECHNOLOGY

Liquid Fertilizers from Superphosphoric Acid and Potassium Hydroxide

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Formulations, salting-out temperatures, and storage properties of liquid fertilizers based on superphosphoric acid and potassium hydroxide are presented. The use of potassium hydroxide permitted the production of high-analysis liquid fertilizers of low-chlorine content, which is desirable for some crops, and the production of neutral solutions of 1:4:4 and 0:1:1 ratios, which could not be made with potassium chloride as the only source of potash. The grades that did not salt out on storage for 1 week at 32° F. were considerably higher than can be made with potassium chloride as the source of potash. Some of the grades were 11–11–11, 7–14–14, 6–18–18, 5–20–20, 10–20–10, 8–24–8, 6–12–18, and 0–25–25.

In earlier reports, information was presented on the production of high-analysis liquid fertilizers from superphosphoric acid (76% P_2O_5) (*1, 2*) and on the use of this acid as a sequestrant to prevent the precipitation of impurities from wet-process phosphoric acid when it is ammoniated (*3*). The potash in the liquid fertilizers was supplied as potassium chloride, which is relatively inexpensive and commonly used in liquid and solid fertilizers.

With a view toward expanding the available information relative to liquid fertilizers and potential raw materials, an experimental study was made of liquid fertilizers based on superphosphoric acid and potassium hydroxide. A recognized drawback to the use of potassium hydroxide in liquid fertilizers is its relatively high cost. However, there may be special situations, especially for crops which need low chlorine fertilizers, where the use of potassium hydroxide or mixtures of potassium hydroxide and potassium chloride may be justified economically. Potassium sulfate, which commonly is used in low-chlorine solid fertilizers, is not sufficiently soluble for use in liquid fertilizers. Use of potassium hydroxide also would permit production of neutral liquids of no- and low-nitrogen grades. Liquids of this type made with potassium chloride would not contain enough ammonia to neutralize the acid and therefore would be highly acidic. Exploratory tests indicated that the use of potassium hydroxide would result in liquids of exceptionally high plant food concentration. Formulations, salting-out and saturation temperatures, and results of storage tests of liquid fertilizers made in the laboratory based on superphosphoric acid and potassium hydroxide are presented.

Laboratory Test Procedure

The liquid fertilizers were made batchwise in a 600-ml. beaker. The potassium hydroxide was added first to the beaker. Agitation then was provided while the superphosphoric acid, water, and ammonia, if needed, were added. If the formulation included solid raw materials such as urea or potassium chloride, these materials were added last. An ice bath was used to maintain the temperature of the reaction below 180° F. This temperature was set as the maximum to prevent excessive evaporation of water, which would result in solutions of concentrations higher than desired.

Salting-out temperatures of the products were determined by cooling the solution at a rate of 4° F. per hour until crystals formed. The solution was then warmed at the same rate until the crystals dissolved to determine saturation temperatures. The maximum grade with a salting-out temperature below 32° F. was determined for each type of solution in the ratios studied. The liquids that had saturation temperatures below 32° F. also were tested in storage for 1 week at 32° F. The crystallizing phases for most of the liquids studied were identified by petrographic analysis. An electronic pH meter was used for pH measurements and a hydrometer was used for specific gravity determinations.

Low-Chlorine Grades. Superphosphoric acid, potassium hydroxide, urea, and water were used in the production of 1:2:2, 1:2:3, 1:3:3, 2:4:5, 1:1:1, 1:2:1, and 1:3:1 ratio fertilizers. These products contained no chlorine. Ammonia was included in formulations for the 1:2:1 and 1:3:1 ratios, since the amount of potassium hydroxide was not sufficient to neutralize the acid. Also, since it is believed that the application of less than about 40 pounds of chlorine per acre would not be detrimental to tobacco, liquid fertilizers of several ratios were made with part of the potash supplied

Table I. Effect of Source of Potash on Maximum Grades of Liquid Fertilizer Made with Superphosphoric Acid

	Maximum Grade of Liquid Fertilizer Made with Indicated Source of Potash[a]				
Ratio	*KOH*	*1/4 KOH 3/4 KCl*	*1/2 KOH 1/2 KCl*	*2/3 KOH 1/3 KCl*	*KCl*
0:1:1	0–25–25	. . .	. . .	. . .	. . .[b]
1:1:1	11–11–11	. . .	. . .	. . .	9–9–9
1:2:1	10–20–10	. . .	. . .	. . .	8–16–8
1:2:2	7–14–14	. . .	6–12–12	. . .	5–10–10
1:2:3	6–12–18	. . .	. . .	5–10–15	3–6–9
1:3:1	8–24–8	. . .	. . .	. . .	7–21–7
1:3:2	. . .	. . .	5–15–10	. . .	4–12–8
1:3:3	6–18–18	. . .	. . .	5–15–15	3–9–9
1:4:2	. . .	. . .	5–20–10	. . .	. . .[b]
1:4:4	. . .	3–12–12	. . .	. . .	. . .[b]
1:6:6	. . .	. . .	2–12–12	. . .	. . .[b]
2:4:5	6–12–15	. . .	. . .	. . .	. . .

[a] Maximum grade that stored for 7 days at 32° F. and 30 days at room temperature without salting out.

[b] Solution would be highly acidic using potassium chloride as the only source of potash.

Table II. Low-Chlorine Fertilizers Made from Superphosphoric Acid and Potassium Hydroxide

	Formulation, Lb./Ton					*Temperature, ° F.*					
Grade	*H_3PO_4, 76% P_2O_5*	*Ammonia, 82.3% N*	*KOH, 37.7% K_2O*	*Urea, 46% N*	*Water*	*Salt out*	*Saturation*	*Crystalline Phase*	*Crystallized during Storage for 1 Week at 32° F.*	*pH*	*Specific Gravity at 85° F.*
					1:1:1 Ratio						
10–10–10	263	. .	531	435	771	15	18	. .	No	7.0	1.270
11–11–11	290	. .	584	478	648	30	32	Urea	No	7.2	1.286
12–12–12	316	. .	636	522	526	47	51	. .	Yes	7.2	1.317
13–13–13	342	. .	690	565	403	65	68	. .	Yes	7.3	1.355
					1:2:1 Ratio						
9–18–9	474	73	477	261	715	0	4	. .	No	7.0	1.278
10–20–10	526	81	531	290	572	22	26	Urea	No	6.9	1.361
11–22–11	579	89	584	319	429	51	56	Urea	Yes	7.3	1.400
					1:2:2 Ratio						
5–10–10	263	. .	531	217	989	12	14	H_2O	No	7.2	1.206
6–12–12	316	. .	637	261	786	6	8	H_2O	No	7.2	1.250
7–14–14	368	. .	743	304	585	5	10	H_2O	No	7.4	1.316
8–16–16	421	. .	849	348	382	36	39	Urea	Yes	7.5	1.380
					1:2:3 Ratio						
5–10–15	263	. .	796	217	724	1	2	. .	No	11.5	1.275
6–12–18	316	. .	955	261	468	15	20	. .	No	11.9	1.364
7–14–21	368	. .	1114	304	214	56	58	. .	Yes	11.9	1.430
					1:3:1 Ratio						
7–21–7	553	113	371	102	861	6	8	. .	No	6.7	1.295
8–24–8	632	130	424	116	698	−4	−2	H_2O	No	6.7	1.360
9–27–9	711	146	477	130	536	87	92	Urea	Yes	7.3	1.474
					1:3:3 Ratio						
3–9–9	237	. .	477	130	1156	18	20	. .	No	7.0	1.172
4–12–12	316	. .	637	174	873	12	13	. .	No	7.1	1.255
5–15–15	395	. .	796	217	592	−1	+1	. .	No	7.2	1.330
6–18–18	474	. .	955	261	310	26	29	. .	No	7.4	1.408
7–21–21	553	. .	1114	304	29	65	71	. .	Yes	7.4	1.505
					2:4:5 Ratio						
4–8–10	211	. .	531	174	1084	15	16	. .	No	8.3	1.174
6–12–15	316	. .	796	261	627	−2	0	. .	No	8.9	1.310
7–14–18	368	. .	955	304	373	35	40	. .	Yes	10.1	1.390

as potassium chloride. Calculations showed that, at the normal rate of application of 80 to 100 pounds of K_2O per acre for tobacco, the fertilizer could contain half of its potash as potassium chloride and half as potassium hydroxide without exceeding the limit of 40 pounds of chloride. At an application rate of 150 pounds of K_2O per acre, the fertilizer could contain about one third of its potash as potassium chloride.

Table I shows the maximum grades of liquid fertilizers of various ratios that did not salt out when subjected to the standard storage tests (7 days at 32° F. and 30 days at room temperature). Also included in the table are the maximum grades that can be made with all the potash supplied as potassium chloride.

The data show that, in general, the most concentrated solutions were obtained when all the potash was supplied as potassium hydroxide and supplemental nitrogen was supplied as urea. The products were two to three grades higher than can be made from ammonia, urea, superphosphoric acid, and all the potash supplied as potassium chloride. Providing potash as mixtures of potassium hydroxide and potassium chloride rather than all potassium hydroxide usually decreased the concentration one grade.

Table II shows formulations, salting-out and saturation temperatures, and other data for liquid fertilizers made from superphosphoric acid, potassium hydroxide, and urea. All the products were essentially neutral (pH, 7.0 to 7.5) except those of 1:2:3 and 2:4:5 ratios, which were of high pH (8.3 to 11.9) because of their high ratio of K_2O to P_2O_5. The caustic nature of the latter products would not present any serious corrosion problems with mild steel tanks and equipment; however, aluminum equipment would not be suitable.

For the ratios tested, the salting-out temperatures decreased and then increased as the concentration of the product increased. Water was the crystallizing phase at the lower concentrations and increasing the concentration depressed the freezing point. Urea crystallized at the higher concentrations.

The small differences between salting-out and saturation temperatures shown in the table indicate that there was some supercooling during salting-out determinations or overheating during saturation determinations. However, the accuracy is believed to be sufficient for practical application in production of the grades listed. None of the solutions with saturation temperatures below 32° F. crystallized during storage for 1 week at 32° F.

Table III shows the data for products made with some of the potash supplied as potassium hydroxide and the remainder as potassium chloride. Such formulations are of interest since they would meet the requirement for low-chlorine content as stated earlier and would be less expensive per unit of plant nutrient than formulations in which all the potash is supplied as potassium hydroxide.

The ratios studied were 1:2:2 and 1:3:2 in which half of the potash was supplied as potassium chloride and 1:2:3 and 1:3:3 in which one third was supplied as potassium chloride. Except for the 1:2:3 ratio formulations, the amount of potassium hydroxide was not enough to neutralize the acid so some of the nitrogen was supplied as ammonia. The remainder of the nitrogen was supplied as urea or urea–ammonium nitrate solution (28.6% N).

As pointed out earlier, supplying some of the potash as potassium chloride usually increased the salting-out temperatures. Also, for most ratios, the salting-out temperatures usually were higher when nitrogen was supplied as urea–ammonium nitrate solution instead of as urea. A 7–14–14 solution with all the potash supplied as potassium hydroxide withstood the storage tests, but a 6–12–12 was the highest satisfactory grade when potassium chloride was included in the formulation. The maximum grade was further reduced to a 5–10–10 when urea–ammonium nitrate solution was used as the source of supplemental nitrogen. However, as shown in Table I, grades produced with these formulations were higher than can be produced when all the potash is supplied as potassium chloride.

Table III. Low-Chlorine Grades Made from Superphosphoric Acid, Potassium Hydroxide, and Potassium Chloride

	Formulation, Lb./Ton							Temperature, ° F.					
Grade	Urea, 46% N	Urea-ammonium nitrate solution, 28.6% N[a]	Ammonia, 82.3% N	H_3PO_4, 76% P_2O_5	KOH, 37.7% K_2O	KCl, 62% K_2O	Water	Salt out	Saturation	Crystalline Phase	Crystallized during Storage for 1 Week at 32° F.	pH	Specific Gravity at 85° F.
One Half K_2O as KCl, 1:2:2 Ratio													
6–12–12	174	..	49	316	318	193	950	0	1	H_2O	No	6.8	1.279
7–14–14	203	..	57	368	371	226	775	52	56	KCl	Yes	6.8	1.332
5–10–10	..	233	40	263	265	161	1038	23	27	KCl	No	6.5	1.238
6–12–12	..	280	49	316	318	193	844	49	52	KCl	Yes	6.6	1.289
7–14–14	..	326	57	368	371	226	652	66	70	KCl	Yes	6.6	1.351
1:3:2 Ratio													
5–15–10	72	..	81	395	265	161	1026	1	3	H_2O	No	6.6	1.276
6–18–12	87	..	97	474	318	193	831	35	38	KCl	Yes	6.6	1.339
5–15–10	..	116	81	395	265	161	982	9	12	H_2O	No	6.5	1.280
6–18–12	..	140	97	474	318	193	778	34	38	KCl	..	6.5	1.346
One Third K_2O as KCl, 1:2:3 Ratio													
5–10–15	217	..	..	263	531	161	828	−3	+1	H_2O	No	6.5	1.287
6–12–18	261	..	..	316	637	193	593	51	55	KCl	Yes	7.0	1.355
3–6–9	..	210	..	158	318	97	1217	18	20	H_2O	No	6.6	1.171
4–8–12	..	280	..	210	424	129	957	37	40	KNO_3	Yes	6.6	1.234
5–10–15	..	350	..	263	531	161	695	58	62	KCl	Yes	6.6	1.302
6–12–18	..	420	..	316	637	193	434	Room temperature		KNO_3	Yes	..	..
1:3:3 Ratio													
5–15–15	145	..	40	395	531	161	728	19	22	KCl	No	6.9	1.341
6–18–18	174	..	49	474	637	193	473	Room temperature		KCl	Yes	..	..
4–12–12	..	93	65	316	424	129	973	26	28	KCl	No	6.6	1.270
5–15–15	..	233	40	395	531	161	640	55	57	KCl	Yes	6.6	1.355

[a] 30.5% urea, 39.5% ammonium nitrate.

Table IV. No-Nitrogen and Low-Nitrogen Fertilizers Made from Superphosphoric Acid, Potassium Hydroxide,[a] and Potassium Chloride

	Formulation, Lb./Ton					Temperature, ° F.					
Grade	H_3PO_4, 76% P_2O_5	Ammonia, 82.3% N	KOH, 37.7% K_2O	KCl, 62% K_2O	Water	Salt out	Saturation	Crystalline Phase	Crystallized during Storage for 1 Week at 32° F.	pH	Specific Gravity at 85° F.
						0:1:1–1.3 Ratio					
0–25–25	658	..	1326	..	16	−14	−13	H_2O	No	7.1	1.561
0–26–26[b]	684	..	1316	..	..	Room temperature		KH_2PO_4	Yes	..	..
0–29–31[c]	763	..	849	..	388	<−15	..	..	No	7.8	1.725
0–27–36[c]	711	..	986	..	303	<−15	..	..	No	11.4	1.785
						1:4:2 Ratio					
4–16–8	421	97	212	129	1141	8	10	H_2O	No	6.6	1.254
5–20–10	526	121	265	161	927	6	13	KCl	No	6.6	1.312
6–24–12	632	146	318	193	711	..[d]	..	KCl	..	..	..
						1:4:4 Ratio					
3–12–12	316	73	159	290	1162	31	35	KCl	No	6.6	1.256
4–16–16	421	97	212	387	883	..[d]	..	KCl	Yes	..	..
						1:6:6 Ratio					
2–12–12	316	49	318	193	1124	7	8	H_2O	No	6.6	1.248
3–18–18	474	73	478	290	685	..[d]	..	KCl	Yes	..	..

[a] Potassium hydroxide used only in that amount necessary to obtain a neutral solution, except for 0:1:1 ratio.
[b] Used 47% KOH solution.
[c] Used solid KOH (73% K_2O).
[d] Did not go into solution.

The crystalline phase for the solutions tested was usually water for salting-out temperatures of near 0° F. or below. Above 32° F., the crystallizing phase was urea for solutions made with potassium hydroxide and was usually potassium chloride for those made with mixtures of potassium hydroxide and potassium chloride. For salting-out temperatures between 0° and 32° F., the crystals formed were either water or salt (urea or potassium chloride) depending on whether the freezing point was depressed or the salt solubility was exceeded.

Low-Nitrogen Grades. Another interesting application for potassium hydroxide in liquid fertilizers is in production of neutral no- and low-nitrogen ratios such as 0:1:1 and 1:4:4. Such ratios made from acid and potassium chloride would not contain enough ammonia to neutralize the P_2O_5 present and therefore would be highly acidic.

Information on solutions with a 0:1:1 ratio prepared from superphosphoric acid and potassium hydroxide is shown in Table IV. A 0–25–25 grade was the most concentrated with an exact 0:1:1 ratio that salted out below 32° F. Water was the crystallizing phase. A 0–26–26 salted out at room temperature and potassium dihydrogen phosphate was the crystallizing phase. Liquids of maximum plant food content can be produced from superphosphoric acid and potassium hydroxide when the P_2O_5:K_2O ratio is slightly less than 1. This is illustrated by the 0–29–31 and 0–27–36 grades shown in Table IV with salting-out temperatures below −15° F. With orthophosphoric acid and potassium hydroxide, the maximum grade with a salting-out temperature below 32° F. for a 0:1:1 ratio is 0–14–14.

Table IV also shows data for low-nitrogen ratios such as 1:4:2, 1:4:4, and 1:6:6. All of the nitrogen in these formulations was supplied as ammonia and only enough potassium hydroxide was added to produce neutral solutions. The remainder of the potash was derived from potassium chloride. For the ratios studied, the amount of K_2O from potassium hydroxide was one fourth to one half of the total. The maximum grades that did not salt out at 32° F. were 5–20–10, 3–12–12, and 2–12–12 for the respective ratios. The crystalline phase was potassium chloride for the 5–20–10 and 3–12–12 grades, and water for the 2–12–12 grade. The amount of potassium chloride required to produce the next higher grade at each ratio would not dissolve at room temperature. A 5–20–20 grade (not shown in the table) with all the potash supplied as potassium hydroxide and with all of the nitrogen supplied as urea had a salting-out temperature of 18° F. and urea was the crystallizing phase.

Discussion

Based on observations made during laboratory work and during a few tests in a 5-gallon reactor, potassium hydroxide was used successfully in a commercial liquid fertilizer plant. No difficulties were encountered.

Although the use of potassium hydroxide is limited because of its present high cost, it must be considered an important potential raw material because of the special grades and high analyses products that can be made.

Since this work has been completed, potassium carbonate has become available at a lower cost than potassium hydroxide. Presumably, the carbonate can be substituted for an equivalent amount of hydroxide in some of the formulations.

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Literature Cited

(1) Striplin, M. M., Jr., McKnight, David, Megar, G. H., J. Agr. Food Chem. **6**, 298–303 (1958).
(2) Striplin, M. M., Jr., Stinson, J. M., Wilbanks, J. A., *Ibid.*, **7**, 623–8 (1959).
(3) Wilbanks, J. A., Nason, M. C., Scott, W. C., *Ibid.*, **9**, 174–8 (1961).

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