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Effects of Surface Active Agents on Properties of Superphosphates and Mixed Fertilizers

The announcement in 1952 that surfactants improve the physical condition of mixed fertilizers resulted in the widespread use of such agents by the fertilizer industry. Conflicting results, however, soon emphasized the need for systematic study of their behavior in fertilizers. The present paper gives the results of such a study with seven different surfactants representing nonionic and anionic types. Nonionic surfactants decreased and anionics increased the bulk density of superphosphate by over 13% when added during acidulation of rock. Ammonia-absorption efficiencies of superphosphates prepared with surfactants added during acidulation were 1 to 9% higher than those of the corresponding reference superphosphates. Caking tendencies of mixed fertilizers were decreased by as much as 45% with use of nonionics during acidulation and increased by as much as 37% with use of anionics. Surfactants added during preparation of mixed fertilizer were about half as effective as the same surfactants added during acidulation. Surfactants apparently do not have properties that ensure elimination of caking in fertilizers under the variable conditions encountered in commercial practice.

THE TREND TOWARD PRODUCTION of high-analysis mixed fertilizers has been accompanied by increased awareness of such problems as bag caking, ammonia loss, and reversion of phosphorus pentoxide. The use of surface active agents as a possible remedy for these and other problems has been of considerable interest to the fertilizer industry since late 1952. Early claims suggested that as little as 0.5 pound of surfactant per ton of fertilizer would aid ammonia penetration of superphosphate particles without affecting phosphate availability, accelerate curing reactions in mixtures, and reduce secondary caking in bagged materials (13). Detailed information on the specific effects of surfactants in superphosphates and mixtures is still extremely meager and in many instances conflicting reports on the behavior of surfactants have been made (3, 4, 12).

Laboratory studies by Fox, Batson, and Breen (7) have shown that surfactants added during acidulation of phosphate rock may improve the physical character of the superphosphate and its ease of removal from the den. The work reported here is an extension of these studies to show the effect of surfactants added during acidulation of rock and before ammoniation of cured superphosphate, on the properties of the products and their mixtures with other fertilizer materials.

Surfactants

Seven of the numerous surfactants currently marketed for use in fertilizers

were selected for the present study. They represented both anionic and nonionic types with variations in structure reported to influence their wetting and detergent characteristics (6, 14). Chemical descriptions and appropriate laboratory numbers are shown in Table I.

Superphosphates

The reference superphosphates used in the study were 20- to 40-mesh (0.833- to 0.381-mm.) size fractions of two ordinary superphosphates and two triple superphosphates prepared 3 months earlier in

the laboratory. Their chemical compositions are shown in Table II. Ordinary superphosphate, OS-3155, was prepared from a commercial grade of Florida land-pebble rock (a blend of washer pebble and double-floated concentrate), while ordinary superphosphate, OS-3156, was prepared from nonfloated Florida land-pebble rock. Triple superphosphate (concentrated superphosphate), TS-3157, was prepared from double-floated Florida land-pebble concentrate and wet-process phosphoric acid. TS-3160 was a triple superphosphate prepared from non-floated Idaho rock and wet-process acid.

Table I. Classification of Surfactants

Lab. No.	Type	Active Ingredient
A-1	Anionic	Dodecylbenzene sodium sulfonate
A-2	Anionic	Tripropenyl-naphthalene sodium sulfonate
A-3	Anionic	Dodecylbenzene triethanolamine sulfonate
A-4	Anionic	Sodium 2-ethylhexyl sulfate
N-1	Nonionic	A condensation product of tridecyl alcohol with ethylene oxide
N-2	Nonionic	A condensation product of an alkylphenol with ethylene oxide
N-3	Nonionic	Alkylphenoxy polyhydroxy ethylene ethanol

Table II. Chemical Composition of Reference Superphosphates

Lab. No.	Superphosphate ^a Type	Phosphorus Pentoxide, %				Free Acid ^b (as H ₃ PO ₄), %	Fluorine ^c , %
		Total	Citrate-insoluble	Available	Water-soluble		
OS-3155	Ordinary	23.13	0.63	22.50	21.20	0.81	1.62
OS-3156	Ordinary	22.70	0.87	21.83	20.53	0.69	1.97
TS-3157	Triple	50.59	0.33	50.26	48.17	2.27	2.16
TS-3160	Triple	49.41	2.32	47.09	43.84	1.34	1.72

^a Particle size, 20-40 mesh.

^b Acetone extraction method (9).

^c Method of Reynolds and Hill (11).

The acidulation equipment consisted of a Ross Change-Can mixer equipped with 8-gallon stainless steel cans, cover, and mixing blade (7). Surfactants in appropriate amounts were either pre-mixed with the acid or added directly to the rock. Agents A-1, A-2, A-3, and N-3 which were incompatible with the acid solution were added to the rock in the mixing can, whereas acid-soluble agents N-1 and N-2 were mixed with the acid solution prior to its addition to the rock. Surfactant A-4 was not included in this series of tests.

Equipment and Procedure

Ammonia-absorption efficiencies of superphosphates were determined by a method described in an earlier paper (10). The ammoniator, a steel drum 7 inches wide and 14 inches in diameter, was rotated at 30 r.p.m. Three inclined 1-inch cross flights aided in turnover of the material as anhydrous ammonia was injected through a nozzle inserted in the hollow trunnion of the drum. Temperature of the reaction was measured by an iron-constantan thermocouple attached to a recorder.

Absorption tests were conducted on 600-gram batches of ordinary superphosphates and 400-gram batches of triple superphosphates previously wetted to 6.5% moisture and stored in closed containers for 24 hours. Anhydrous ammonia equivalent to 6 pounds per 20 pounds of available phosphorus pentoxide in the case of ordinary superphosphate and 4 pounds per 20 pounds of available phosphorus pentoxide in the case of triple superphosphate was dispensed from a steel buret equipped with a sight glass. The ammonia was added uniformly for 2 minutes and another 2 minutes was allowed for further mixing and absorption. Ammoniations were initiated at room temperature (about 78° F.). Maximum temperatures of reaction varied from about 140° F. for ammoniation of ordinary superphosphate to about 160° F. for ammoniation of triple superphosphate. After discharge, the batch was exposed to air for 5 minutes to permit escape of unreacted ammonia. Analytical samples were obtained after 24 hours. Standard AOAC methods of analysis were used for determinations of free moisture (air-flow procedure), nitrogen, and phosphorus pentoxide (5). Bulk-density measurements were obtained by weighing the amount of loosely packed material contained in a cylinder of known volume.

The effect of surfactants on caking tendency of mixed fertilizers was determined by conducting laboratory caking tests using the general method of Adams and Ross (7, 2). Cakes 1 inch in thickness and 2 inches in diameter were formed under a pressure of 12 pounds per square inch in caking bombs stored for 7

Table III. Formulas of Caking-Test Mixtures

Ingredient	Mixture			
	10-11-10	10-10-10	11-25-11	11-23-11
	Pounds per ton			
Superphosphate	1000	1000	1000	1000
Anhydrous ammonia, 82.3% N	67	65	101	94
Ammonium nitrate, 33.0% N	176	184	225	255
Ammonium sulfate, 20.5% N	423	417	307	284
Potassium chloride, 60.0% K ₂ O	334	334	367	367
Total	2000	2000	2000	2000

days at 86° F. and 40% relative humidity. After removal, cakes were dried in an air oven at 122° F. for 72 hours. The drying procedure reduced the moisture content of cake to less than 0.5% and ensured cementation of fertilizer particles. Crushing strengths of cakes were measured by means of a hydraulic press.

All solid ingredients of the fertilizer mixtures were prescreened to give size fractions of 20- to 40-mesh. Formulations of the mixed fertilizers were based on a 50% dilution of the superphosphates maintaining at the same time a 1 to 1 ratio for the N-K₂O contents. A 10-11-10 fertilizer was formulated from the OS-3155 superphosphate, a 10-10-10 fertilizer from the OS-3156 superphosphate, an 11-25-11 mixture from the TS-3157 superphosphate, and an 11-23-11 mixture from the TS-3160 superphosphate. Formulas are shown in Table III. In order to standardize moisture and surfactant contents of caking-test mixtures, all superphosphates were ammoniated prior to batching of the fertilizers.

Surfactants Added during Acidulation of Rock

Fox *et al.* (7) showed that superphosphates prepared with the inclusion of nonionic surfactants during acidulation of rock exhibited less den set than the reference superphosphates, and that inclusion of anionic surfactants in the preparation of superphosphates did not materially alter the hardness of the denned material. Data supplementing their results and showing bulk densities and ammonia-absorption efficiencies of the cured superphosphates, as well as caking tendencies of mixed fertilizers containing these superphosphates, are shown in Table IV.

Bulk densities of superphosphates containing nonionic surfactants added during acidulation were generally lower than those of their respective reference superphosphates. Those of superphosphates prepared with inclusion of anionic surfactants were somewhat higher. In the case of TS-3157 superphosphate prepared from double-floated Florida land pebble concentrate and having a bulk

Table IV. Properties of Superphosphates and Mixed Fertilizers Prepared with Surfactants Added during Acidulation of Rock

Lab. No.	Superphosphate			Mixed Fertilizer	
	Surfactant ^a added	Bulk density ^b , lb./cu. ft.	Ammonia-absorption efficiency, %	Grade ^c	Crushing strength of cake ^d , lb./sq. in.
OS-3155	None	48.0	87.3	10-11-10	93
	A-1	49.9	89.1	10-11-10	109
	A-2	49.8	92.2	10-11-10	105
	A-3	51.1	90.2	10-11-10	..
	N-1	..	89.3	10-11-10	..
	N-2	46.1	91.8	10-11-10	94
	N-3	49.5	93.2	10-11-10	..
OS-3156	None	48.0	81.5	10-10-10	36
	A-3	49.7	83.9	10-10-10	39
	N-1	45.0	85.0	10-10-10	22**
	N-3	45.8	82.6	10-10-10	21**
TS-3157	None	40.8	83.4	11-25-11	51
	A-1	46.2	86.3	11-25-11	70**
	N-1	36.7	89.4	11-25-11	48*
	N-2	36.9	92.4	11-25-11	41**
	N-3	37.1	90.4	11-25-11	49
TS-3160	None	42.3	86.1	11-23-11	78
	N-1	36.0	89.0	11-23-11	66**
	N-3	35.6	87.7	11-23-11	64**

^a 0.75 lb. of active ingredient per ton of superphosphate.

^b Average results of duplicate determinations. All differences between surfactant-treated and corresponding untreated materials are significant at 1% level.

^c Moisture content of 10-11-10 mixture, 3.8%; 10-10-10, 3.2%; 11-25-11, 5.7%; 11-23-11, 5.3%.

^d Average results of 5 replicate tests. Significant differences between surfactant-treated and corresponding untreated materials: *, 5% level, **, 1% level.

Table V. Effect of Surfactants Added during Mixing Phase on Ammonia-Absorption Efficiency of Cured Superphosphates

Surfactant	Active Ingredient Added, Lb./Ton Superphosphate		
	0.0	0.75	1.50
Ammonia-Absorption Efficiency, %			
Superphosphate OS-3156 ^a			
None	85.0
A-1	..	88.9	87.2
A-2	..	87.5	88.0
A-3	..	89.6	87.2
A-4	..	88.4	88.8
N-1	..	87.2	87.9
N-2	..	87.5	88.9
N-3	..	84.5	88.0
Superphosphate TS-3160 ^b			
None	86.1
A-2	89.4
A-3	89.5
N-1	88.0
N-3	87.4

^a Particle size, -10-mesh; ammonia added, 6 lb./20 lb. available P₂O₅.

^b Particle size, 20-40-mesh; ammonia added, 4 lb./20 lb. available P₂O₅.

density of 40.8 pounds per cubic foot, the inclusion of surfactants N-1, N-2, and N-3 in amounts equivalent to 0.75 pound of active ingredient per ton of superphosphate reduced the density to 36.7, 36.9, and 37.1 pounds per cubic foot, respectively. The inclusion of the same amount of active ingredient as anionic surfactant A-1 raised the density of the superphosphate to 46.2 pounds per cubic foot.

Absorption efficiency refers to the percentage of ammonia absorbed in terms of that added. Absorption efficiencies of superphosphates containing surfactants added during acidulation were 1.1 to 9.0% higher than those of the reference superphosphates. Superphosphate OS-3156 containing surfactant N-3 absorbed 82.6% of the ammonia added as compared to 81.5% for its reference superphosphate, while TS-3157 containing surfactant N-2 absorbed 92.4% as compared to 83.4% for its reference material. The increases are of the same order of magnitude as those resulting from the reduction of the particle size of superphosphates from 20-40 to minus 80-mesh (10). However, no definite advantage was apparent in use of any one type or class of surfactant over another and no correlation was found between bulk densities and ammonia-absorption efficiencies. A previous paper (10) has shown that denseness of superphosphate particles is a factor contributing to low ammonia absorption. The present data indicate that surfactants tend to counteract this effect of bulk density on ammonia absorption.

The effect of surfactants added during acidulation of rock on caking tendency of the final mixed fertilizer is also shown in Table IV. Reductions in crushing strength of cakes were obtained with use

of nonionic surfactants during acidulation and increases were obtained with use of anionics. The changes in crushing strengths are attributed to variations in density of the superphosphates directly caused by the addition of surfactants during their preparation. Differences in crushing strengths of the four reference mixtures are attributable to differences in formulation and initial moisture content of the mixtures (Tables III and IV) and to physical differences of the superphosphates other than density, as indicated by their ammonia absorption efficiencies. The maximum reduction in crushing strength (from 36 to 21 pounds per square inch) occurred with the 10-10-10 mixture containing a nonionic surfactant (N-3) added during preparation of the superphosphate. This

Table VI. Effect of Surfactants Added during Mixing Phase on Caking Tendency of Mixed Fertilizer

Surfactant ^a	Crushing Strength of Fertilizer Cake ^b , Lb./Sq. In.
10-10-10 ^c containing superphosphate OS-3156	
None	36
A-1	34
A-2	39
A-3	37
A-4	38
N-1	35
N-2	37
N-3	40
11-23-11 ^d containing superphosphate TS-3160	
None	78
A-2	79
A-3	75
N-1	78
N-3	80

^a Active ingredient, 0.75 lb. per ton of fertilizer.

^b Average results of five replicate determinations.

^c Moisture content, 3.2%.

^d Moisture content, 5.3%.

reduction in crushing strength is comparable to that attained by the addition of 100 pounds of an inert conditioner, such as fuller's earth, per ton of mixed fertilizer (8).

Surfactants Added during Mixing Process

In plant practice surfactants may logically be introduced either during acidulation of rock in the preparation of superphosphate or during the mixing phase in the processing of mixed goods. Surfactants added during the latter phase may be batched with the solid ingredients or, in the case of nonionic types which are primarily liquid, may be introduced directly into the mixer with the nitrogen solution.

Test lots of cured superphosphate were treated 24 hours prior to ammoniation with water solutions or suspensions of surfactants in concentrations and amounts

calculated to give a moisture content of 6% and active ingredient contents of 0.75 and 1.5 pounds per ton of superphosphate. Absorption efficiencies of superphosphates OS-3156 and TS-3160 with and without surfactant additions are shown in Table V. Both superphosphates treated with 1.5 pounds of active ingredient per ton of superphosphate showed general increases in absorption efficiencies amounting to 2 to 3%. Superphosphate OS-3156 treated with 0.75 pound of the various active ingredients per ton showed that some surfactants were as effective when added at that rate as when added in larger amounts. Others, principally the nonionics and in particular surfactant N-3, were much less effective when added at the lower rate.

The effect of varying amounts of surfactants on ammonia-absorption efficiencies of superphosphates is shown in Figure 1. Section A shows the effect of varying amounts of surfactants added during acidulation and section B that of the same surfactants added to the cured superphosphates. Surfactant A-3 is slightly more effective than either N-1 or N-3 at the lower concentrations and less effective than the others at the higher concentrations. N-3, which is the least effective at the lower concentrations, is the most effective at the higher level. The curves also indicate that surfactants added during acidulation have a greater effect on the ammonia-absorption efficiencies of superphosphates than when added just prior to ammoniation. The effects shown for 1.5 pounds of the active ingredients added to the cured superphosphate are roughly equivalent to those shown for the addition during

Table VII. Solubilities of Phosphorus Pentoxide in Ammoniated Ordinary Superphosphate Treated with Surfactants

Lab. No.	Surfactant ^a Active ingredient, lb./ton superphosphate	Phosphorus Pentoxide ^b , % of Total P ₂ O ₅	
		Water-soluble	Citrate-insoluble
None	..	35.7	9.2
A-1	0.75	33.4	9.9
A-1	1.50	34.9	10.1
A-2	0.75	33.9	9.3
A-2	1.50	34.6	10.3
A-3	0.75	31.7	8.6
A-3	1.50	35.3	9.1
A-4	0.75	34.5	9.9
A-4	1.50	34.6	10.6
N-1	0.75	34.4	9.5
N-1	1.50	33.6	9.2
N-2	0.75	35.2	9.7
N-2	1.50	34.5	9.2
N-3	0.75	35.9	8.3
N-3	1.50	35.2	9.2

^a Surfactants added 24 hours prior to ammoniation.

^b Analyses obtained from ammoniated superphosphate OS-3156 (ammoniation rate 6 lb. NH₃/20 lb. P₂O₅) containing 5% moisture and stored for 30 days at 86° F.

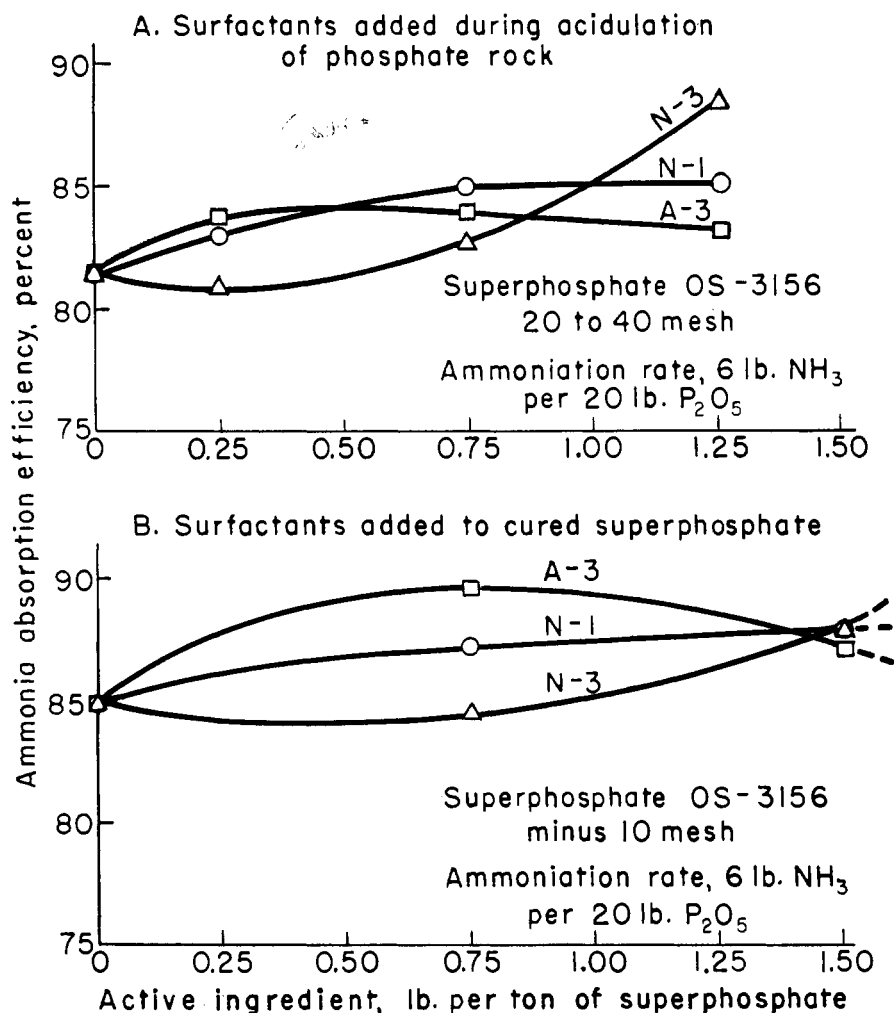


Figure 1. Effect of varying amounts of surfactants on ammonia absorption efficiency of ordinary superphosphate

acidulation of 0.75 pound of active ingredients. The greater effectiveness of surfactants added during acidulation of rock may be attributed to the more effective dispersion afforded by the slurry mixing involved in acidulation than in the relatively dry mixing occurring during ammoniation. The higher absorption efficiency shown for reference superphosphate in section B as compared to that in section A is due to difference in particle size of the superphosphates.

The effect of surfactants added during the mixing phase on caking tendency of mixed fertilizers is shown in Table VI. None of the surfactants tested showed any significant alterations in the caking tendency of either a 10-10-10 mixture containing superphosphate OS-3156 or an 11-23-11 mixture containing superphosphate TS-3160.

Effect of Surfactants on Phosphorus Pentoxide Solubility in Superphosphates

Analyses of ammoniated superphosphates gave no indication that surfactant treatments affect the solubilities of phosphorus pentoxide in superphosphates. Table VII shows the water-soluble and citrate-insoluble phosphorus

pentoxide contents of 30-day-old ammoniated superphosphate OS-3156 with and without additions of surfactants 24 hours prior to ammoniation. The samples contained approximately 5% moisture during storage at 86° F.

Treated superphosphates had water-soluble phosphorus pentoxide contents ranging from 31.7 to 35.9% of the total phosphorus pentoxide as compared to 35.7% for the reference superphosphate. Citrate-insoluble phosphorus pentoxide contents of treated superphosphates ranged from 8.3 to 10.6% of the total phosphorus pentoxide as against 9.2% for the untreated material. These variations are in accord with those shown by replicated ammoniations and 30-day storage tests of superphosphates (70).

Summary

Seven different surfactants were selected as representative of a large number of such agents currently marketed for use in mixed fertilizers. A study has been made of the effects of these surfactants on densities and ammonia-absorption efficiencies of ordinary and triple superphosphates and on caking tendencies of mixed fertilizers.

Nonionic surfactants added during acidulation of rock in amounts equivalent to 0.75 pound of active ingredient per ton of superphosphate decreased the bulk densities of 20-40-mesh size-fractions of cured superphosphates as much as 13.5%, whereas anionic surfactants increased the bulk densities as much as 13.2%.

Ammonia-absorption efficiencies of superphosphates prepared with surfactants added during acidulation were 1 to 9% higher than those of the corresponding reference superphosphates. No correlation was found between absorption efficiencies and bulk densities.

Nonionic surfactants added during acidulation decreased the crushing strength of mixed fertilizer cake as much as 45%, whereas anionics increased the crushing strength as much as 37%. Good correlation was found between bulk density of the superphosphate used in the fertilizer and the crushing strength of the fertilizer cake.

Surfactants added during the mixing phase in amounts equivalent to 1.5 pounds of active ingredient per ton of superphosphate increased ammonia-absorption efficiencies of the superphosphates as much as 4% but did not affect crushing strengths of the mixed fertilizer cakes. The amounts of active ingredients required during the mixing phase for maximum individual effectiveness as regards improvement of ammonia absorption varied from 0.75 to over 1.5 pounds per ton of superphosphate.

Surfactants added during acidulation were about twice as effective as those added during the preparation of the mixed fertilizer.

No evidence of general superiority was found among the individual members of either the anionic or the nonionic groups.

Surfactants had no effect on the water-soluble or citrate-insoluble phosphorus pentoxide contents of ammoniated superphosphates stored for 30 days.

In general, maximum effects from use of surfactants may be obtained with the addition of proper amounts of nonionic surfactants during superphosphate manufacture and these effects may take the form of lower density of superphosphate, moderate increases in ammonia-absorption capacity, and slightly better physical condition of the bagged fertilizer.

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SURFACTANTS IN FERTILIZER

Sorption of Surface Active Agents from Aqueous Solution by Phosphate Rock

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The adsorption of surface active agents from aqueous solutions by phosphate rock suspensions has been investigated as a possible clue to previously reported differences between the behaviors of nonfloated and double-floated phosphate rocks during acidulation. Changes in surfactant concentration as measured by differences in relative surface tensions of the solutions before and after contact with the rock indicate that the anionic, nonionic, and cationic types of surfactants are adsorbed on the surface of rock particles in varying degrees depending on the type and molecular complexity of the surfactant, the particle size and the degree of surface saturation of the rock, and on the previous treatment of the latter with one or more flotation reagents. The presence of the cationic reagent used in the flotation process doubtlessly explains the enhanced reaction rates observed in the acidulation of double-floated rock.

IN A PREVIOUS INVESTIGATION of the use of anionic and nonionic surface active agents in phosphate rock acidulation, double-floated rock behaved like washer pebble rock treated with an effective surface active agent (1, 4). In the double-flotation process, phosphate rock is floated with an anionic-type reagent in the first stage. The cationic surfactant used in the second stage is a flotation agent for siliceous material and a depressant for phosphate rock. It has generally been assumed that relatively little, if any, of the cationic reagent is retained in the rock product. The present investigation was initiated to determine whether the presence of surfactants could be detected in the rock by surface tension procedures. The presence of the anionic-type flotation reagent in single-floated rock has already been demonstrated by other means (3).

Procedure

In preliminary experiments, aqueous and acetone extracts of double-floated rock exhibited substantially the same surface tension as the pure solvents. Consequently, attempts to demonstrate the presence of surface active agents in the rock by this procedure were ineffective. The procedure of measuring the surface tension of aqueous surfactant solution before and after contact with phosphate rock suspensions, however, showed significant differences and has been used in this investigation of the sorption of different types of surfactants by phosphate rock from several sources.

Aqueous solutions of various concentrations of surfactants, expressed as percentage active ingredient, were prepared and measurements of the solution surface tension were made by the capillary-

rise method. For this purpose graduated thermometer stems open at both ends were used. The capillaries were cleaned with acetone and water after each solution measurement and checked for reproducibility of results against distilled water. Repeated checks agreed within limits of experimental error of about 1% with the surface tension of water at the temperature of observation. Since the results were expressed as relative surface tension, close control over temperature was not necessary, and the surface tension measurements of the surfactant solutions were made at prevailing room temperatures, which varied over the range, 25° to 32° C., corresponding to a change of about 1.4% in the surface tension of water.

Measurements were made by drawing the solutions through the capillaries to wet the walls and expel entrapped air,