Evaluation of Effects of Surfactants in Fertilizer Manufacture

F. A. RETZKE,
G. F. SACHSEL, and
R. B. FILBERT, JR.
Battelle Memorial Institute, 505 King Ave., Columbus 1, Ohio

Simple tests for solubility, stability, and foaming of surfactants in sulfuric acid and ammonium hydroxide, and similar tests for effects on surface tension of sulfuric acid, were found to be of doubtful value for screening surfactants. The effect of surfactants on ultimate phosphorus pentoxide conversion was negligible. Bag-storage tests with 3–12–12 having surfactant added at various stages of production showed a slight and somewhat inconsistent benefit with some surfactant treatments.

THE USE OF SURFACTANTS to reduce caking of fertilizer, very briefly explored by two of the authors in 1951 (and rejected in favor of certain conditioners), started receiving startling publicity in 1952 (*1, 3–5, 10*). These early reports claimed that the curing of superphosphate as well as of ammoniated goods was speeded by the use of surfactants, and that the physical condition of the resulting mixed goods was very good, even after short storage periods. Field experiences reported the following year (*1, 6, 9*) showed mixed results, ranging all the way from very beneficial effects to no effect at all. None of the reports published in 1952 and 1953 presented sufficient data to make possible an easy decision on the merits of surfactants in this application.

The authors, therefore, undertook an evaluation of a number of surface-active agents with a twofold purpose: to attempt to select, by simple laboratory experiments, from the large number of products on the market, a few for large scale tests in a fertilizer plant; and to perform large scale acidulation and ammoniation runs in the plant with a few selected surfactants and examine the manufactured products.

Laboratory Experiments

Screening Tests

It is not easy to blend a pound of additive with a ton of fertilizer with the equipment and procedures of the average fertilizer plant, particularly when the additive is a solid. To get reasonably good distribution of a surfactant in commercial manufacture of fertilizer, it should be added to the solids in the form of a solution or dispersion of reasonably large volume. In the case of superphosphate, this meant 56° or 58° Bé. sulfuric acid, and for ammoniation it meant any one of a number of commercial ammoniating solutions containing ammonium hydroxide, ammonium nitrate, and sometimes urea. Mixing, particularly when cutback water is added to the sulfuric acid, is often accomplished by bubbling air into the liquid. With these facts in mind, the following variables were studied in the laboratory in an attempt to screen surfactants, by means of simple tests, for possible plant use:

Solubility and stability of surfactant in acid and alkaline solutions.

Amount of foaming in acid and alkaline solutions of surfactant with moderate air agitation.

Effect of surfactant on the surface tension of acid solutions.

Effect of surfactant on percentage of available phosphorus pentoxide and on rate of conversion of unavailable phosphorus pentoxide to the available form of plant food.

The solutions used were 58° Bé. sulfuric acid and aqua ammonia containing 28.5% ammonia. The amount of acid or alkaline solution and the amount of surfactant mixed with this solution were proportional to the amounts of these materials which have been recommended for use in a ton of wet superphosphate or mixed fertilizer.

Screening Results

Solubility, Stability, Foaming, and Surface Tension. All of the 32 surfactants screened were found to be soluble in sulfuric acid and ammonium hydroxide. A separate liquid phase appeared in some of the acid solutions, but subsequent surface-tension tests suggested that the appearance of a separate phase in itself did not necessarily indicate instability.

When air was bubbled through the

Table I. Surfactants Selected for Detailed Evaluation

Surfactant No.	Type	Trade Description	Foaming Test: Acid	Foaming Test: Alkali	Surface Tension in Acid	Lab. Acidulation test	Plant Scale Tests
1	A	Alkyl aryl sulfonate	P	F	P	√	
7	A	Alkyl aryl sulfonate	P	F	P	√	
8	A	Alkyl aryl sulfonate	P	F	F	√	
9	A	Alkyl aryl sulfonate	P	F	P	√	√
15	N	Condensate of ethylene oxide and polyoxy propylene	P	F	F	√	
19	A	Alkyl aryl sodium sulfonate	P	F	P	√	
20	A	Alkyl aryl sodium sulfonate	P	F	N.t.	N.t.	√
21	A	Alkyl aryl sodium sulfonate	P	N.t.	P	√	√
28	N	Salt of monoalkyl phosphoric ester	P	P	P	√	

A. Anionic.
N. Nonionic.
P. Passed test (see text for criteria).
F. Failed test (see text for criteria).
N.t. No test.
√. Used in test.

Table II. Summary of Phosphate Conversion for Laboratory Acidulation Tests

Surfactant Data		Active agent, %	Apparent Surface Tension in Sulfuric Acid, Dynes/Cm.	Equivalent Concn. Lb.[a]/Ton	Conversion after Cure, %
					3 Days
15[b]	N	100	41.5	1.5	94.5
21	A	75	32.9	2.0	96.8
28	N	100	28.6	1.5	97.4
					5 Days
1	A	40	32.9	3.7	94.8
7	A	40	31.8	3.7	94.2
8[b]	A	40	36.1	3.7	94.3
9	A	85	32.7	1.8	94.6
19	A	35	32.8	3.7	93.8
Control			74.2		96.2
					13 Days
1	A	40	32.9	3.7	93.7
7	A	40	31.8	3.7	94.0
8[b]	A	40	36.1	3.7	94.8
9	A	85	32.7	1.8	94.9
19	A	35	32.8	3.7	93.6
Control			74.2		95.9

[a] Designed to give, in each case, active agent concentration equivalent to 1.5 lb. per ton of superphosphate.
[b] Did not pass surface tension test.

acid solutions, 15 of the 32 surfactants gave foam volumes at least twice as great as those of the other 17. Application of the same criterion to the 17 surfactants that gave relatively low foam volumes in acid solution left only two materials, both nonionics, that gave relatively low foam volumes in both sulfuric acid and ammonium hydroxide.

Surface-tension experiments with a Cenco-Du Noüy surface tensiometer showed that commercial chamber acid itself had surface tensions varying from 74.2 to 48.2 dynes per cm. at 100° F. Filtration of this acid eliminated the variation and gave readings comparable to those of C.P. reagent sulfuric acid. Even in commercial chamber acid, 10 out of the 17 "low-acid foamers" gave surface tension readings of 33 dynes per cm. or less, substantially below the lowest crude chamber acid value observed.

Table I describes the nine surfactants that were further evaluated and indicates how they had been rated as to foaming and ability to lower surface tension of sulfuric acid.

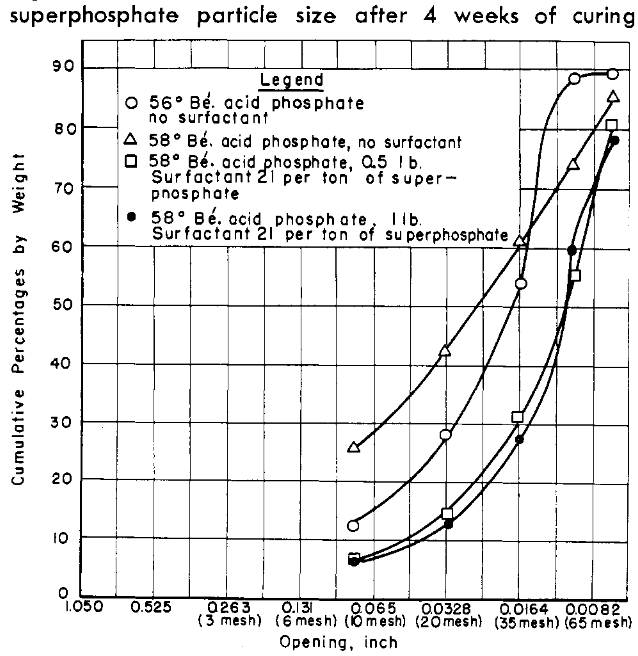
Acidulating Studies Eight of the nine surfactants listed in Table I were subjected to laboratory acidulating experiments. These included two materials that had shown a negligible reduction in the surface tension of sulfuric acid.

Normal superphosphate was made in 1664-gram batches in the laboratory, and samples were analyzed for phosphorus pentoxide. The acid-to-rock ratio used in the laboratory tests was the same as commercial operation—0.81. The commercial 58° Bé. sulfuric acid containing the desired concentration of surfactant was heated to about 100° F. and then added to the phosphate rock. The material was mixed with a planetary-type kitchen mixer for 2 minutes, the approximate conventional plant scale mixing time. After the batch had been mixed, it was transferred to a glass jar and stored at 77° F. and 50% relative humidity for curing.

The first three batches were analyzed after 3 days' curing. The remaining five batches were sampled and analyzed twice, after 5 and 13 days. Table II shows the percentage of phosphorus pentoxide conversion. In the first series there was some indication that the surfactant rejected from the surface tension test gave a lower conversion than two surfactants that had passed the test. The second series did not show any such difference. As a matter of fact, the control batch, made with surfactant-free acid, gave a higher conversion than any of the five batches containing surfactant.

Of the eight surfactants examined, only No. 21, an alkyl aryl sodium sulfonate, and No. 28, a salt of a monoalkyl phosphoric acid ester, showed some slight promise in aiding phosphorous pentoxide conversion.

Figure 1. Effect of surfactant and acid concentration on superphosphate particle size after 4 weeks of curing



Plant Tests

Although it would have been desirable to repeat, extend, and refine the laboratory tests, the need for an early schedule on plant tests required a selection on the basis of the data described above.

A study of these data, and the cost of various suitable surfactants, resulted in the selection of No. 21 for large scale acidulating runs. For ammoniation, selection was dictated by the following facts: Surfactant 20 had been used in the plant previously on an empirical basis without any evaluation; surfactant 9 was the only material available in a commercial ammoniating solution.

Four distinct types of plant tests were made. The first two were acidulating tests with and without surfactants. The other two were ammoniation runs using superphosphate made with and without surfactants, and either adding or not adding a surfactant before or during ammoniation. The purpose of this scheme was to find out if surfactants were more effective when used in acidulation or in ammoniation, or whether they should be used in both steps, or not at all.

Acidulation Four 65-ton dens of normal superphosphate were according to the formulas shown in Table III. The acid and rock were mixed in a conventional pan mixer. The surfactant when used was dissolved in a minimum amount of water and added to the acid in the acid-dilution tanks. Air agitation of this mixture did not cause foaming. A dark, oily layer appeared on the surface of the acid-surfactant solution. No difficulty was experienced in pumping this solution, mixing it and the rock, or cutting the resulting superphosphate from the den.

Qualitative observations made during the curing period of the piles indicated that the pile made with surfactant-free 58° Bé. acid was the hardest. In general, differences in hardness between the piles containing surfactants and the 56° Bé. acid pile were very slight. Pile temperatures, observed during the first 14 days of curing, did not differ appreciably.

As shown in Figure 1, sieve analyses of samples from the piles indicated that superphosphate containing 1 pound of surfactant per ton had the finest particle size, while that made with surfactant-free 58° Bé. acid was the coarsest.

Moisture analyses during a 4-week curing period showed that the superphosphate made with 58° Bé. acid contained less moisture than that made with 56° Bé. acid. Surfactants did not appear to have an effect on the moisture content of the superphosphate. These results are shown in Table III.

The free acid content of all the superphosphate made with 58° Bé. acid was less than that made with 56° Bé. acid. In general, the free acid content was lower in the superphosphate containing the higher concentration of surfactant.

Based on analyses of superphosphate samples taken immediately after ex-denning, initial phosphate conversion was more rapid in mixtures containing the higher concentration of surfactant. This effect had previously been reported by Fox and others (7). However, after the superphosphate had cured for 1 to 4 weeks, phosphate conversion was generally lower in the material containing surfactants. This would indicate that the surfactants used did not decrease the curing time or increase the phosphate conversion of the superphosphate in the pile.

Mixed Fertilizer Mixed 3–12–12 fertilizer was made by the conventional batch process with superphosphate from the test piles. Five 15-ton piles of fertilizer were made after a 2-week curing period for the super-

Table III. Chemical Analysis of Superphosphate from Plant Runs

Pile No.	Sulfuric Acid, ° B'.[a]	Surfactant 21, Lb./Ton[b]	Weight Per Cent: Moisture	Free acid	P_2O_5 Available	P_2O_5 Insoluble	P_2O_5 Total	Conversion, %
								After Ex-denning
1	56	0	7.70	2.85	19.20	1.00	20.20	95.1
2	58	0	6.40	2.54	19.40	1.00	20.40	95.1
3	58	0.5	6.10	2.22	19.60	1.10	20.70	94.7
4	58	1.0	5.50	2.54	19.70	0.75	20.45	96.3
								After Pile Curing, 1 Week
1	56	0	7.90	1.90	19.45	0.65	20.10	96.8
2	58	0	5.20	2.22	19.55	1.00	20.55	95.1
3	58	0.5	5.30	1.90	19.40	1.10	20.50	94.6
4	58	1.0	6.20	2.22	19.95	0.95	20.90	95.5
								2 Weeks
1	56	0	8.80	2.54	19.35	0.40	19.75	98.0
2	58	0	7.40	2.54	19.65	0.40	20.05	98.0
3	58	0.5	6.10	1.90	20.00	0.50	20.50	97.6
4	58	1.0	6.90	1.58	20.00	0.55	20.55	97.3
								3 Weeks
1	56	0	7.80	1.90	19.75	0.35	20.10	98.3
2	58	0	5.90	1.58	20.30	0.45	20.75	97.8
3	58	0.5	5.80	1.58	20.20	0.50	20.70	97.6
4	58	1.0	6.50	1.90	20.10	0.40	20.50	98.1
								4 Weeks
1	56	0	8.60	2.22	19.60	0.25	19.85	98.7
2	58	0	6.50	1.90	19.90	0.35	20.25	98.2
3	58	0.5	6.50	1.90	20.30	0.50	20.80	97.6
4	58	1.0	7.20	1.58	20.05	0.55	20.60	97.3

[a] 915 lb. sulfuric acid and 1085 lb. 75% BPL phosphate rock per wet ton superphosphate for pile 1; all other piles 895 lb. acid and 1105 lb. rock.
[b] Wet superphosphate basis.

Table IV. Comparison of Phosphate Conversion in Superphosphate and 3–12–12 Fertilizer in Plant Tests

Mixed fertilizer, pile No.	Manufacturing Conditions: Superphosphate: Sulfuric acid concn., ° Bé.	Surfactant 21 added to acid, lb./wet ton superphosphate	Curing time, days	Mixed Fertilizer, Surfactant Added during Mixing: No.	Lb./ton mixed fertilizer	Phosphate Conversion Data: In superphosphate before mixing	In mixed fertilizer after 2-week pile curing	Change in % conversion
1	56	...	14	20	1.0	98.0	94.3	−3.7
2	58	...	14	..	...	98.0	96.0	−2.0
3	58	0.5	14	..	...	97.6	95.6	−2.0
4	58	0.5	14	20	0.5	97.6	94.9	−2.7
5	58	1.0	14	..	...	97.3	95.5	−1.8
6	56	...	28	20	1.0	98.7	97.9	−0.8
7	58	...	28	..	...	98.2	97.2	−1.0
8	58	0.5	28	..	...	97.6	96.4	−1.2
9	58	0.5	28	20	0.5	97.6	98.4	+0.8
10	58	0.5	28	9	0.28	97.6	96.1	−1.5
11	58	1.0	28	..	...	97.3	95.0	−2.3
12	58	1.0	28	9	0.28	97.3	96.7	−0.6

Table V. Abridged Record of Bag-Storage Tests

Mixed Fertilizer, Pile No.	Moisture When Bagged, Wt. %	Rating[a] after Bag Storage		
		2 weeks	4 weeks	8 weeks
Bagged after 1 Week of Pile Curing				
1[b]	6.50	5	6 (2)	7 (2)
2	5.50	5	5 (2)	7 (3)
3	5.30	5	7 (2)	7 (2)
4	5.10	6	7 (3)	7 (4)
5	6.10	5	7 (2)	7 (3)
6[b]	6.60	7 (2)	7 (2)	7 (5)
7	6.60	6 (2)	7 (3)	7 (4)
8	6.30	7 (2)	7 (4)	7 (3)
9	5.10	7 (1)	7 (2)	7 (3)
10	5.50	...	7 (3)	7 (3)
11	6.20	7 (1)	6 (3)	7 (4)
12	6.00	5	7 (1)	6 (2)
Bagged after 2 Weeks of Pile Curing				
1[b]	5.90	7 (1)	7 (2)	7 (1)
2	5.20	7 (2)	7 (3)	7 (2)
3	5.20	7	7 (3)	7 (2)
4	5.30	7	7 (2)	7 (3)
5	5.70	7 (2)	7 (4)	7 (2)
6[b]	5.50	7 (1)	7 (3)	5 (1)
7	5.30	7 (2)	7 (2)	7 (2)
8	5.40	7 (2)	7 (2)	7
9	5.80	7 (1)	7 (4)	7 (3)
10	5.90	...	7 (4)	5 (1)
11	5.60	5 (1)	6 (2)	4 (1)
12	4.90	5 (1)	6 (1)	5 (3)

[a] Free-flowing material with no lumps was rated 1. Material with lumps 12 inches and above was rated 7; and material with lumps of smaller size was assigned intermediate ratings. Ratings shown outside parentheses are for bag 7 (not dropped), numbered downward from top of an 8-bag stack; numbers in parentheses refer to bag 8, which was dropped four times from waist height, once on each side.
[b] Inert silicate conditioner added at time of bagging.

phosphate and seven 15-ton piles were made after a 4-week curing period. The general conditions are shown in Table IV, together with the phosphorus pentoxide conversion results.

Surfactant 20, used in making four piles, was scattered on top of the other ingredients in the boot of the elevator to the mixer. Surfactant 9, used in making two other piles, was mixed with the nitrogen solution. Only a slight amount of foaming was observed in the solution measuring tank, and no operating difficulties were experienced in the mixer using the surfactant-nitrogen solution.

Differences in the hardness of the 12 piles were found to be slight. Pile temperatures, observed only during the first week of pile storage, did not differ appreciably. Sieve analyses of samples taken after mixing indicated no significant differences in the particle-size distribution.

Comparison of the phosphate conversion in the superphosphate before ammoniation with the phosphate conversion in the mixed fertilizer, after 2-week pile curing (shown in Table IV), suggested that:

The decrease in phosphate conversion as a result of mixing was less in mixed fertilizer made with 4-week cured superphosphate than in that made with 2-week cured superphosphate, whether surfactants were used or not.

Surfactant 20 added at the time of manipulation had no benefit on phosphate conversion in mixed fertilizer containing 2-week cured superphosphate. Some slight benefit from its use resulted with 4-week cured superphosphate. The effects of surfactant 9 were not apparent.

There was no benefit gained from carry-over effect to the mixed fertilizer by doubling the concentration of surfactant 21 in the preparation of superphosphate.

It is possible that the effects on phosphate conversion, observed after acidulation and after mixing, may be ascribed to the fact that the anionic surfactant used in the plant produced undesirable effects because of the presence of an effective cationic flotation reagent on the phosphate rock. The effects for such a case have been reported, and discussed in detail by Fox, Hardesty, and Kumagai (*8*). Unfortunately, no data were available on the history of the phosphate rock used in the authors' tests; thus no definite conclusion could be drawn.

Bag Storage

A portion of each mixed fertilizer pile was bagged after the material had cured in the pile for 1 or 2 weeks. An inert conditioner was added at the time of bagging to the mixed goods containing superphosphate made with 56° Bé. acid. Three-ply bags were used, one ply of which was asphalt-laminated. The bags were stored in stacks of eight bags each in a weatherproof (unheated) storage building. Inspections were made after 2, 4, and 8 weeks, starting in early January 1954 and terminating in early March 1954. At the time of inspection, all bags were carefully lowered to the ground. The bottom bag was dropped once on each side (four drops altogether) from waist height. The bags were then opened and rated in terms of the size of the largest lump. Table V shows the rating for the bottom bag, which was dropped four times, and the bag above it, which was not dropped.

The results did not point to any quantitative conclusion regarding the effect of any variable on caking. Some general observations can be made, however.

All materials were badly caked when rough handling was avoided.

Even when the dropped bags were examined, no material was found to be consistently free-flowing.

Among the dropped bags, only some of those containing some surfactant were found to be entirely free-flowing.

The differences in ratings between various surfactant treatments seemed to be as great as the differences between piles containing 2- or 4-week-old superphosphate.

Effects of pile curing before bagging, although erratic at times, were often about as great as the difference between surfactant treatments.

In previous work with granulated goods (*2*), undisturbed bottom bags in eight-bag stacks had been found to be substantially free-flowing after extended storage. This was not the case with any of the materials examined in this series of experiments.

Literature Cited

(1) *Agr. Chemicals*, **8,** No. 6, 48–9 (1953).
(2) Battelle Memorial Institute, unpublished data.
(3) *Chem. Processing*, **15,** No. 11, 36–8 (1952).
(4) *Chem. Week*, **71,** No. 19, 9 (1952).
(5) *Ibid.*, **71,** No. 21, 50–2 (1952).
(6) *Ibid.*, **72,** No. 22, 52–5 (1953).
(7) Fox, E. J., Batson, H. E., Jr., and Breen, A. V., J. Agr. Food Chem., **2,** 618–23 (1954).
(8) Fox, E. J., Hardesty, J. O., and Kumagai, R., *Farm Chemicals*, **117,** No. 9, 43, 45, 47 (1954).
(9) Sauchelli, V., *Agr. Chemicals*, **8,** No. 11, 32–4, 143, 145, 147 (1953).
(10) Seymour, J. E., "Use and Effect of Surface Active Agents in Manufacture of Mixed Fertilizer," American Farm Research Association, Osage Beach, Mo., Oct. 20 and 21, 1952.

Received for review September 7, 1954. Accepted April 8, 1955. Presented before the Division of Fertilizer and Soil Chemistry, Symposium on Fertilizer Technology, at the 126th Meeting of the American Chemical Society, *New York, N. Y., 1954.*