SURFACTANTS IN FERTILIZERS

Use of Surface Active Agents in Phosphate Rock Acidulation

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The effects of anionic and nonionic types of surface active agents on the reaction phenomena during the acidulation of phosphate rock were studied in the laboratory to obtain information on their influence in industrial practice. The surfactants tended to accelerate the primary reaction between phosphate rock and sulfuric acid, but had no significant effect on the extent of the over-all reaction in the period of 1 to 24 hours after mixing. The physical character of the product denned 20 hours at 70° C. was altered in varying degrees depending upon the type and chemical composition of the surfactant, the type of rock and the method of ore dressing used in its production, and the type of superphosphate produced. Results obtained in this study indicate the need for a comprehensive examination of the problem of surfactant use in fertilizer technology.

THE USE OF SURFACE ACTIVE AGENTS in the manufacture of fertilizers has been of considerable interest (1, 3) since the presentation of Seymour's article on the use of such agents in mixed fertilizer preparations (6). Widespread use of surfactants in fertilizers without adequate preliminary investigation of their specific effects has created much confusion concerning the possible benefits that may be derived from their use. Accessible information on the nature of the effects of such reagents on the chemical reactions involved in the preparation of fertilizer materials and on the physical characteristics of the products is extremely limited. A laboratory study was undertaken to provide needed information pertaining to the potentialities of surfactant use in superphosphate manufacture. The work has been restricted mainly to observations on 15-pound lots of superphosphate during the first 24 hours after mixing. The effort has been directed toward a determination of the nature and magnitude of specific effects of the surfactants under controlled conditions of acidulation and denning. Their subsequent effects on the curing and ammoniation of the superphosphate and on

the physical and chemical properties of mixed fertilizers are not reported here.

Materials

The chemical and screen analyses of four ground phosphate rocks used in this study are given in Tables I and II. Technical grade sulfuric acid and wet-process phosphoric acid made with virgin sulfuric acid were used in the preparation of the test superphosphates. The sulfuric acid was diluted from 93% (66° Bé.) to 72% (56.5° Bé.) and allowed to cool to room temperature before use.

The phosphoric acid, which carried the phosphorus pentoxide equivalent of 80.9% orthophosphoric acid, contained titratable free acid (to methyl orange) equivalent to 74.5% phosphoric acid. It was diluted to 67.7% strength on the basis of titratable acid at the time of use.

Four each of the anionic and nonionic types of surfactants (supplied by five different producers) were used (Table III). This set of agents appears to be a fairly representative cross section of currently available materials offering possibilities for use in the acidulation of phosphate rock. Agents of the anionic

type, though in more abundant supply at the present time (4, 5), are generally incompatible with strong sulfuric acid solutions in the sense that the liberated organic acid, being sensibly insoluble, separates as a scum on the surface of the acid solution and adheres to the walls of the container. The nonionic types, however, were deemed more suitable for use in the acidulation of phosphate rock because they are miscible with acids. Three of the four nonionics are soluble in water and acid. The fourth (G), an alkyl phenoxy polyoxyethylene ethanol, is an insoluble emulsifier, which produces stable suspensions in acid solutions.

Aqueous solutions of the surface active agents were all made up to contain 94.5 grams of active ingredient per liter, so that a 10-ml. aliquot per 10 pounds of rock was equivalent to 0.25 pound of surface active agent per ton of ordinary superphosphate.

Equipment and Procedure

The principal pieces of equipment used in these tests consisted of a Toledo scale of 50-pound capacity, and a Ross Change-Can mixer with 8-gallon stain-

Table I. Chemical Composition of Phosphate Rocks

Lot No.	Source of Rock	Character of Rock	CaO, %	P₂O₅, %	F, %	CO₂, %	Calcd. Acid-Rock Ratio[a], Lb. H₂SO₄/ Lb. Rock
3155	Florida land pebble	Commercial acidulation grade	47.5	33.7	3.1	2.9	0.571
3156	Florida land pebble	Washer rock[b]	47.4	33.4	3.8	3.1	0.566
3157	Florida land pebble	Double-floated concentrate	48.7	33.5	4.0	3.7	0.586
3163	Wyoming	Commercial acidulation grade	45.3	32.6	4.1	1.8	0.532

[a] H_2SO_4 equivalent of $(CaO - P_2O_5 - 1/3 F_2)$.
[b] Specially prepared material.

Table II. Screen Analyses of Phosphate Rocks

Percentage of Sample Passing Screen[a]

Lot No.	60-mesh	100-mesh	150-mesh	200-mesh	200-mesh (wet)
3155	99.3	95.3	86.4	78.9	83.9
3156	99.9	91.0	73.5	62.0	70.6
3157	99.9	87.2	67.2	57.9	67.7
3163	99.5	97.0	91.2	73.6	86.4

[a] Tyler series.

Table III. Description of Surface Active Agents

Key Letter	Chemical Name
	Anionic
A	Dodecylbenzene sodium sulfonate
B	Decylbenzene sodium sulfonate
F	Polyalkyl naphthalene sodium sulfonate
H	Alkyl benzene triethanolamine sulfonate
	Nonionic
C	Alcohol–ethylene oxide condensation product
D	Mercaptan–ethylene oxide condensation product
E	Alkyl phenyl polyethylene glycol ether[a]
G	Alkyl phenoxy polyoxyethylene ethanol[b]

[a] Products of reaction of an alkylphenol with ethylene oxide.

[b] Emulsifier forms stable suspensions in water and in acid solutions.

less steel cans, cover, and mixing blades, to which was added a stainless steel thermocouple well with a small thin tip thermally insulated from the larger supporting tube, so that high thermal sensitivity might be achieved (Figure 1).

A drying oven of 6-can capacity, specially designed to circulate heated air over the surface of the charge contained in the cans, was used to quick-cure the product at 70° C. The cured superphosphate was excavated by mounting the can on a motor-driven turntable, which was then tilted to slightly below the horizontal position for insertion of the cutter (Figure 2). The relative hardness of the product was measured by its resistance to cutting by a 3-foot cutter bar pivoted at the middle. The pressure on the cutter was measured by the movement of the opposite end of the bar against spring tension over a graduated scale. Two interchangable bronze springs having pressure ranges of 0 to 5 and 0 to 10 pounds, respectively, were used, depending on the hardness of the product.

In the preparation of test samples of ordinary superphosphate the appropriate quantities of sulfuric acid and surfactant solutions were added to 10-pound batches of phosphate rock in the mixing can. In the case of the Florida pebble rocks (Nos. 3155 to 3157, Table I) a charge of 8 pounds of 56.5° Bé. (72%) acid, equivalent to 5.76 po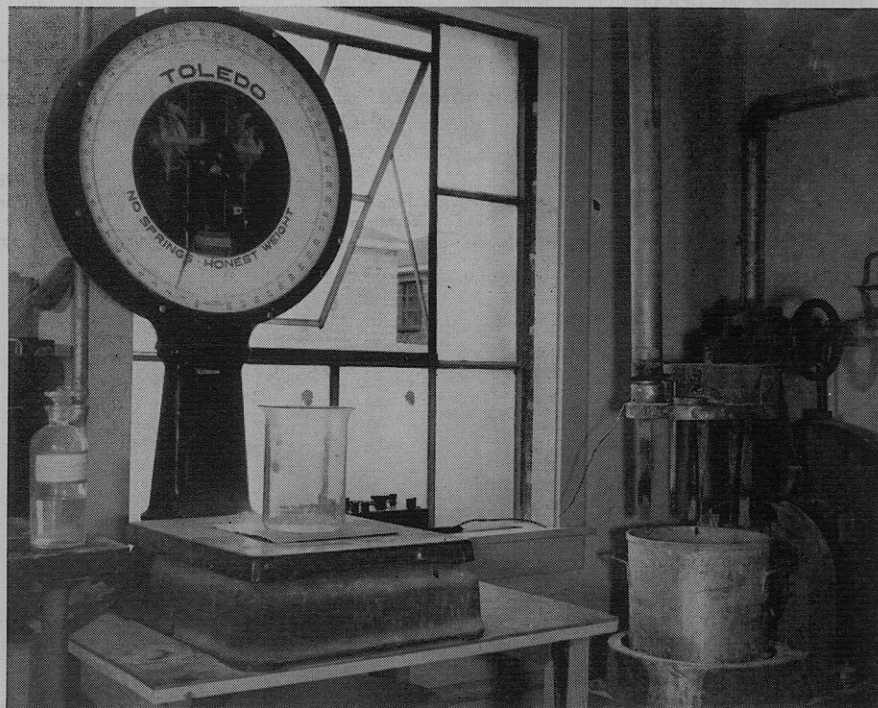unds of sulfuric acid, was used. For the Wyoming rock (No. 3163) the quantity of acid solution was reduced to 7.5 pounds, equivalent to 5.40 pounds of sulfuric acid. When the rate of surfactant addition was less than 50 ml. of solution per 10 pounds of rock (equivalent to 1.25 pounds of surfactant per ton of superphosphate), water was added to keep the volume of solution plus water constant at 50 ml. Surfactants A, B, F, G, and H, which were incompatible with the acid solution, were added to the rock in the mixing can; acid-soluble surfactants C, D, and E and all water additions were mixed with the acid solution previous to its addition to the rock.

The period of agitation in mixtures made with rock 3155 (the first series) was held constant at 2 minutes; but this was reduced to 45 seconds for mixtures made with the other three rocks to prevent overmixing and crumbling of the charge after it had set to a solid condition.

Batch temperatures were recorded at 1-minute intervals until they reached a maximum and started to decline, after which the cover of the mixer was raised and all adhering material was scraped from the mixing blades. The can and its contents were then weighed to determine the weight of the raw mix, and the extent of bloating of the charge was measured. When the 6-can oven was filled, duplicate grab samples (about 2 grams each) of the several charges were weighed, diluted with distilled water, and titrated with standardized sodium hydroxide solution to the end point of methyl orange to determine the residual free acid at this stage (about 1 hour after mixing). This was repeated on 1-gram laboratory samples taken 24 hours later (after curing overnight at 70° C.), at which time the weight of the cured product was determined and the charge was excavated from the can. During the latter procedure, the hardness of the product was determined by measurement of the pressure on the cutting tool shown in Figure 2. Analytical samples, withdrawn in small portions while the excavated products were being mixed in a rotary mixer, were screened to 10-mesh, sealed in screw-cap bottles, and analyzed for residual free acid and citrate-insoluble phosphorus pentoxide (considered as a measure of unreacted rock) the afternoon of the same day. The rest of the materials were stored in fiber drums for future reference, or were discarded.

In the preparation of test concentrated ("triple") superphosphates, the same general procedure was followed, except that the quantity of rock was reduced and the amount of acid solution was increased to yield substantially the same weight of product in which 2 parts by weight of titratable phosphoric acid were substituted for 1 part of sulfuric acid (100% basis) per unit weight of rock and the acid concentration was cut to 67.7% phosphoric acid.

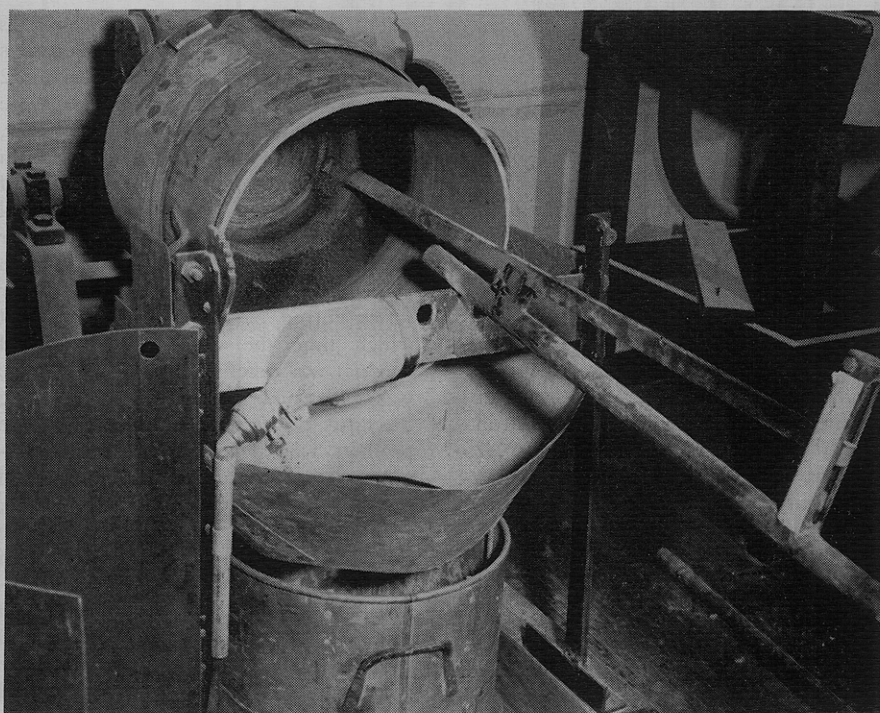**Figure 1. Change-Can mixer with stirrer lifted**

Figure 2. Cured superphosphate being excavated

Cutter pressure is read on calibrated scale mounted on handle of cutting tool

among rocks (item 10). Highly significant differences were found in the effect of surfactant additions on the loss in weight during mixing and during curing and on the hardness of the den product.

The effect of various surfactant additions on the temporary and permanent bloating of the charge during mixing is illustrated in Figure 3. The height of the column shows the maximal temporary depth of the charge, while the heavy line across the column represents the permanent depth of the charge after set. Anionic surfactants F and H (not shown) yielded results similar to those of A and B, while nonionics E and G (not shown) behaved like surfactant C. Surfactant D was an exception in its class or type. In general, the anionics tended to reduce bloating, while the nonionics tended to increase it.

The influence of added surfactants on the rate and extent of the rise in batch temperature is illustrated in Figure 4, in which the temperatures of the control mixtures are indicated by broken curves. The average observed temperatures of three or more tests, regardless of the amount of surfactant added, are represented by solid curves. The data for the commercial acidulation grade of rock 3155 are for a 2-minute stirring period; the others are for a 45-second period. Accelerated heat losses due to the agitation of the mixtures beyond 45 seconds reduced subsequent batch temperatures. When stirring was limited to 45 seconds, the maximal batch temperature in control mixtures made with rock 3155 equaled, or exceeded, that in mixtures made with rock 3157.

The influence of surfactant additions on the loss in weight during mixing and during curing as well as the total loss is shown by the results given in Table V. The percentages given are the maximum

Effects of Surfactants in Ordinary Superphosphate Preparations

Observations were made on the reaction phenomena and on the physical character of the products.

Expansion or bloating of the charge in the mixer.
Pattern of the batch-temperature rise, which reflects the rate and extent of reaction between rock and acid.
Residual free acid in hour-old mix and cured product.
Citrate-insoluble phosphorus pentoxide in the product after curing 24 hours at 70° C.
Weight losses during mixing and curing.
Hardness of the den product in terms of pounds of pressure on the cutting tool while the charge is excavated from the can.

A statistical analysis of the data obtained in the last five observations is summarized in Table IV. Although significant differences were obtained in most categories with respect to the rise in batch-temperature during the first 2 minutes after mixing, there were relatively few significant differences in acid consumption 1 hour after mixing, except as between phosphate rocks; nor in phosphate conversion in the product cured 24 hours at 70° C. except between the amounts of surfactants (item 8), phosphate rocks (item 9), and surfactants

Table IV. Statistical Significance[a] of Differences Between Observations on Test Preparations of Ordinary Superphosphates

| No. | Category of Differences Between | Temp. Rise in Mixer 1st 2 Minutes[b] | Acid Consumption at End of | | Phosphate Conversion at End of 27 hours[e] | Weight Loss | | Hardness of Product Cured 24 Hours at 70° C.[h] |
			1 hour[c]	27 hours[d]		During mixing[f]	During curing[g]	
1	Surfactants and controls	s	n	n	n	n	n	hs
2	Anionics and controls	n	n	n	n	s	n	hs
3	Nonionics and controls	hs	n	n	n	n	s	hs
4	Surfactants	hs	n	n	n	hs	hs	hs
5	Anionics and nonionics	hs	n	n	n	hs	hs	n
6	Anionics	hs	n	n	n	n	n	n
7	Nonionics	hs	n	n	s	n	hs	hs
8	Amounts of surfactants	n	n	s	n	hs	hs	hs
9	Phosphate rocks	hs	hs	hs	hs	hs	hs	hs
10	Surfactants among rocks	hs	n	hs	hs	hs	hs	hs
11	Amounts among surfactants	n	n	n	n	hs	n	n

[a] hs. Highly significant, 1% level. s. Significant, 5% level. n. Not significant.
[b] Temperature increases were 49° to 81° C.
[c] Residual free acid ranged from 1.05 to 2.00 ml. of $1N$ acid per gram of material.
[d] Residual free acid ranged from 0.37 to 0.82 ml. of $1N$ acid per gram of material.
[e] Citrate-insoluble P_2O_5 ranged from 1.30 to 3.60% of cured product.
[f] Weight loss during mixing ranged from 0.35 to 0.86 pound per batch, equivalent to 1.99 to 4.75% of charge.
[g] Weight loss during curing ranged from 0.95 to 1.73 pounds per batch, equivalent to 5.39 to 9.55% of charge.
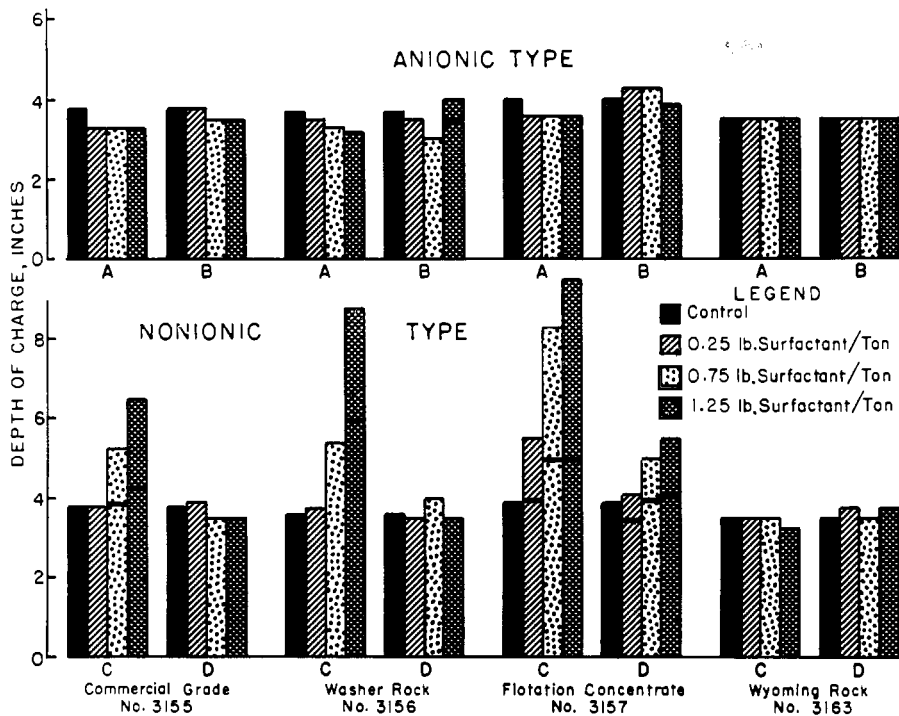[h] Pressure on cutting tool varied from 0.5 to 7.6 pounds.

Figure 3. Effect of surfactants on charge expansion

Permanent expansion is indicated by position of heavy lines on bar graphs

LEGEND
■ Control
▨ 0.25 lb.Surfactant/Ton
▤ 0.75 lb.Surfactant/Ton
▦ 1.25 lb.Surfactant/Ton

and minimum observed over the range 0.25 to 1.25 pounds of surfactant per ton of superphosphate. Surfactants of the anionic type produced no significant difference between the treated and control mixtures during mixing, while three of the four nonionic surfactants showed significant increases in weight loss during the curing period. The influence of the nonionics on weight loss was more pronounced in mixtures made from Florida rock than in those made from western rock.

The data on the influence of 0.25 and 1.25 pounds of surfactant additions per ton on the hardness of the day-old, oven-cured ordinary superphosphates are given in Table VI. In superphosphates prepared from Florida rocks (Nos. 3155 to 3157) the nonionic types of surfactants appear to be more effective in softening the product, whereas in preparations made from western rock (No. 3163) the anionics were slightly superior to the nonionic type. Again, the effectiveness of surfactant additions was more pronounced in superphosphates made from Florida rock than in those made from western rock.

The effect of varying the amount of surfactant added per ton of ordinary superphosphate is illustrated in Figure 5.

Tests made on the use of surfactants in the preparation of concentrated superphosphate from wet-process phosphoric acid (made with virgin sulfuric acid) and Florida land pebble double-float concentrate (No. 3157) yielded the results shown in Figure 6. The control preparations were relatively soft and easily cut, requiring but 4 pounds of pressure

on the cutter blade. Anionic surfactant A, and also F, hardened the product to such an extent that the pressure on the cutting tool exceeded 10 pounds, the limit of the heavy spring. On the other hand, nonionic surfactants C, E, and G

softened the product to such an extent that, in several instances, the superphosphates crumbled and fell from the can before the cutting pressure could be measured. In the preparation of analogous products from a nonfloated western rock (Idaho, No. 3160; 44.4% calcium oxide, 33.2% phosphorus pentoxide, and 3.4% fluorine) the anionic surfactants behaved normally, but did not reduce the hardness of the product to the same extent as did the nonionics.

Discussion

As to the significance of results wherein appreciable differences between control and treated mixtures were obtained, there is still considerable latitude for interpretation. Apparently, the influence of surfactants on the initial rate of reaction between the rock and reagent acid as reflected by the thermal effects shown in Figure 4 did not materially affect the extent of the over-all reaction under the imposed condition of uniform temperature of 70° C. in the curing oven, as shown by the lack of significant variance in acid consumption or phosphate conversion in the products, except between rocks of different physical and chemical composition from various sources. On the other hand, the influence of the surfactants on the physical condition of the product as shown in Table VI and Figures 5 and 6 may affect the drying rate as reflected by the differ-

Figure 4. Effect of surfactants on reaction temperature

Plotted results are averages of observations for three rates used
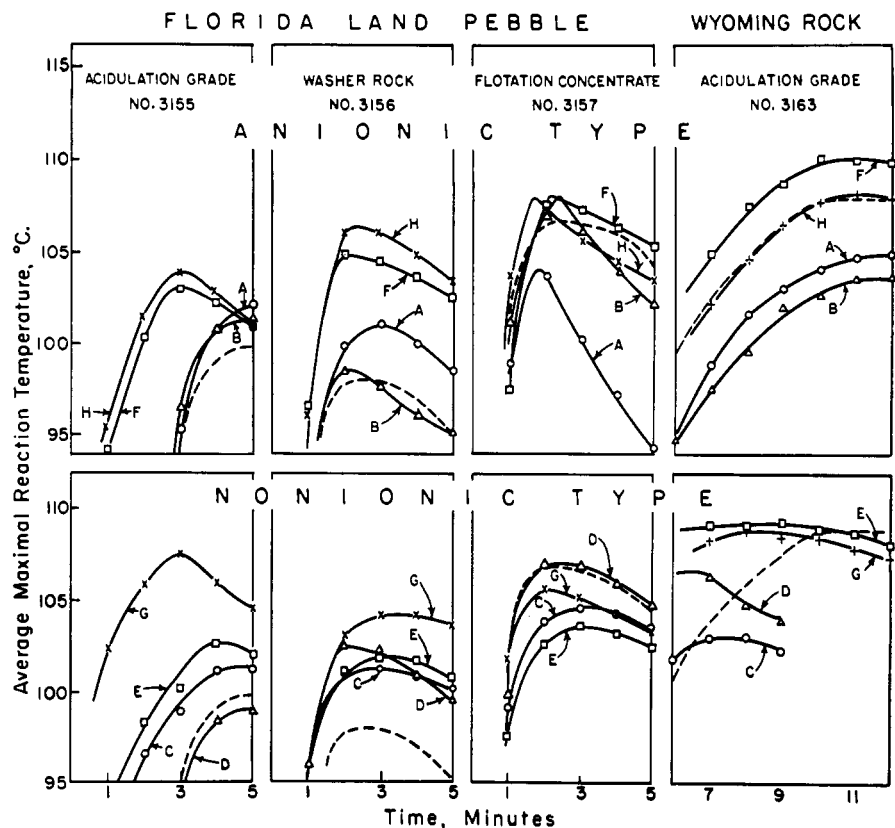
Table V. Influence of Surfactant Additions on Weight Loss During Mixing and Curing of Ordinary Superphosphate Made from Nonfloated Phosphate Rock

| | Weight % of Charge Lost from Preparations Made with | | | | | |
| | Florida Washer Rock 3156 | | | Wyoming Rock 3163 | | |
Type of Mixture	During mixing	During curing	Total	During mixing	During curing	Total
Controls	4.5–4.5	6.1–7.0	10.6–11.5	2.2–2.7	5.7–6.2	8.4–8.4
Anionic surfactants[a]						
A	4.3–4.5	5.7–6.4	10.1–10.9	2.0–2.3	6.1–6.4	8.1–8.7
B	4.5–4.5	5.8–6.1	10.3–10.7	2.6–2.7	5.7–6.0	7.7–8.0
F	4.2–4.8	6.1–6.6	10.6–10.9	2.3–2.3	6.0–6.4	8.4–8.7
H	4.3–4.5	6.4–6.5	10.8–11.1	2.1–2.3	5.8–6.2	8.1–8.3
Av.	4.3–4.6	6.0–6.4	10.4–10.9	2.3–2.4	5.9–6.3	8.1–8.4
Nonionic surfactants[a]						
C	3.9–4.3	7.5–9.6	11.7–13.5	2.5–2.8	5.7–6.2	8.7–9.0
D	4.1–4.6	6.4–6.9	10.8–11.2	2.6–2.7	5.6–6.0	8.6–8.8
E	4.4–4.7	7.1–9.1	11.8–13.6	2.3–3.0	5.7–6.7	8.8–9.3
G	4.4–4.6	7.1–9.3	11.7–13.7	2.5–2.5	6.1–6.1	8.8–8.8
Av.	4.2–4.5	7.0–8.7	11.5–13.0	2.5–2.8	5.8–6.3	8.7–9.0

[a] Figures are minimum and maximum losses without regard to amount of surfactant added.

ence in loss of weight during curing (Table V). It is conceivable that the difference in the drying rate may also affect the rate of phosphate conversion in large factory-scale curing piles, in which event significant differences would be most likely to occur after several days (2).

The influence of the physical and chemical composition of phosphate rocks from various sources was clearly shown by difference in the rate of reaction as reflected in the rate and extent of rise in batch temperature. This is illustrated by the difference in the time required to attain maximal batch temperature in the control mixtures made from Florida washer rock 3156 and Wyoming 3163 (Figure 4). The difference in the rate and extent of the temperature rise in control mixtures made from Florida washer rock (No. 3156) and double-float concentrate (No. 3157) from the same source, however, must be attributed to some factor other than a difference in the fineness of the rock grind, as the screen analyses (Table II) show that the washer rock is slightly finer than the concentrate and therefore should be the more reactive on the basis of rock particle size. The higher calcium carbonate content of the concentrate (Table I) may be partially responsible for its greater reactivity, but, by the same token, the washer rock should show a greater reactivity than the more finely ground commercial acidulation grade (No. 3155). This, however, was not the case. When stirring was limited to 45 seconds, the rate and extent of temperature rise in control mixtures made from commercial rock 3155 equaled, or exceeded, that in mixtures made from the concentrate rock (No. 3157). Furthermore, the abnormal behavior of the anionic surfactants in hardening concentrated superphosphate made from the double-float concentrate, as compared with their normal behavior in softening the product made from nonfloated western rock (Figure 6), is indicative of the influence of some factor in the mixtures made from floated rock that is not present in those made from nonfloated rock. Identification of this factor is one phase of a projected study of varietal differences among commercial phosphate rocks.

As no significant differences attributable to the influence of surfactants in the extent of the over-all reaction were found during 1 to 24 hours after mixing, the usefulness of observations on the thermal phenomena during the primary reaction seems to be limited to an evaluation of the reactivity of rocks from various sources and possibly differentiation between rocks of different physical and chemical composition or previous treatment with flotation reagents.

This leaves observations on the physical character of the product as the most significant measures of the value of surfactant additions in superphosphate preparations, in so far as measurements made in this study are concerned. It is difficult to translate the results obtained in laboratory scale tests into terms applicable to plant scale operations, other than to point out the area wherein significant differences may be expected. The extent of expected beneficiation through altered physical characteristics of the product, obviously, is in direct proportion to the need for improvement in the physical condition of the product. Where products of good physical condition can be produced without surfactants, there is little to be gained by adding them. Conversely, products of poor physical condition may be improved by the use of a suitable surfactant. A striking illustration of the need for improvement is found in the case of concentrated superphosphate made from nonfloated rock.

Summary

An investigation on a laboratory scale has been made of the influence of four

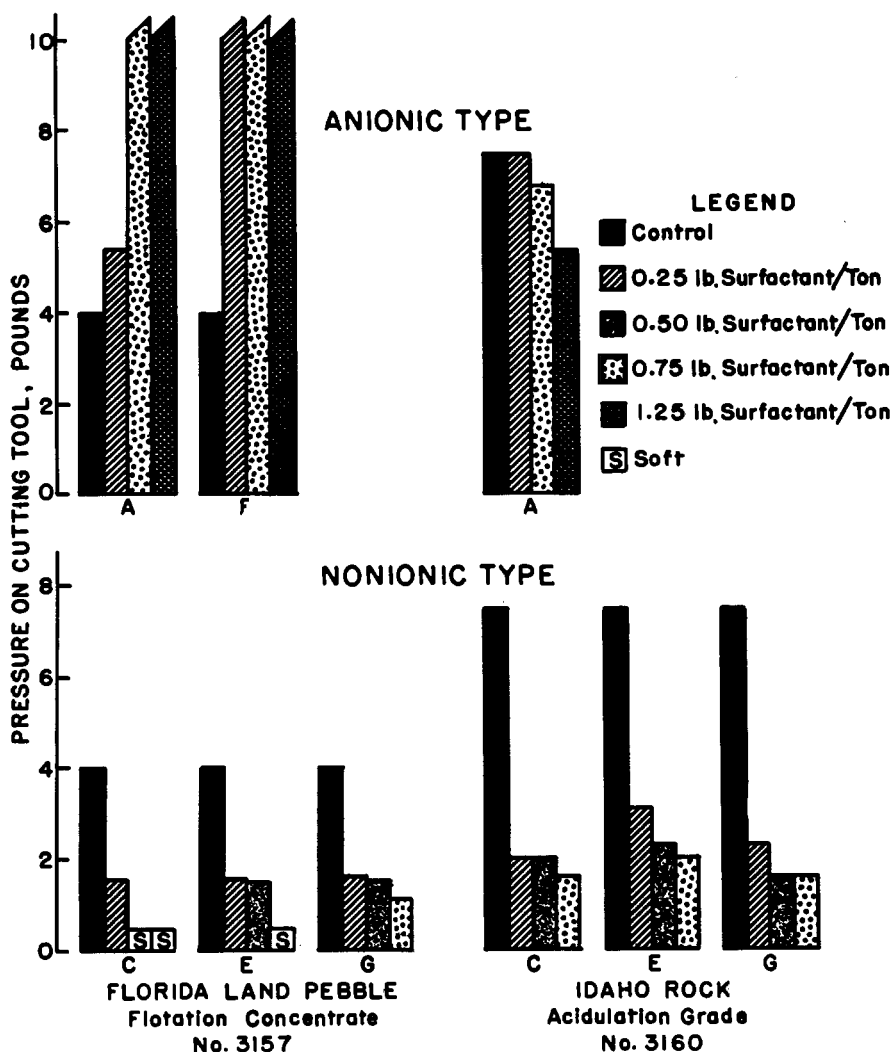**Figure 5. Effect of surfactants on hardness of cured ordinary superphosphate prepared from Florida land pebble**
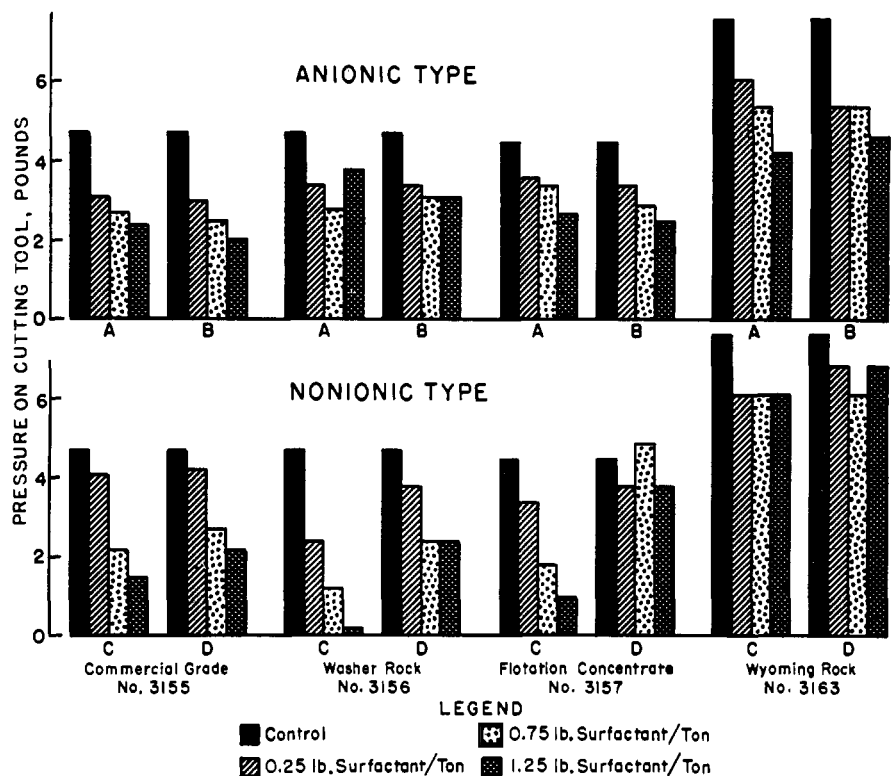
Figure 6. Effect of surfactants on hardness of cured "triple" superphosphate preparations

typical anionic and four nonionic surface active agents on reaction phenomena and on the physical and chemical characteristics of ordinary and concentrated superphosphate preparations made from three Florida and two western rocks. A statistical analysis of the results shows significant differences between control and treated mixtures in measurements on:

Extent of bloating of the charge during mixing.

Rate of initial reaction between the rock and reagent acid.

Rate of drying during curing 24 hours at 70° C.

Hardness of the product.

Other significant differences observed pertained to effects of:

Surfactants of different types.

Surfactants of the same type but different chemical composition.

The reactivity of phosphate rocks from different sources, and from the same source, but of different physical and chemical composition.

No significant differences between control and treated mixtures attributable to the influence of surfactants

were observed in the extent of the overall reaction in day-old, oven-cured products. Beneficial results derived from the use of surfactants were limited very largely to improvement in the

physical character of the products. The acid-stable nonionic type of surfactants generally were more effective than the anionic type. Improvement in the physical condition of concentrated superphosphate was more pronounced than in ordinary superphosphate.

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(3) *Chem. Week*, **71**, No. 21, 50–2 (1952).
(4) *Ibid.*, **72**, No. 22, 52–5 (1953).
(5) Rainey, J. L., and Denoon, C. E., Jr., *Chem. Eng. News*, **31**, 4521–3 (1953).
(6) Seymour, J. E., "Use and Effect of Surface Active Agents in the Manufacture of Mixed Fertilizer," American Farm Research Association Meeting, Osage Beach, Mo., Oct. 20 and 21, 1952.

Table VI. Influence of Surfactant Additions on Hardness of Ordinary Superphosphate Cured 24 Hours at 70° C.

	Rock No.			
	3155	3156	3157	3163
	Pounds of Cutting-Tool Pressure in Products			
Control mixtures	4.2–5.0	4.5–4.8	4.4–4.5	7.6–7.6
Anionic surfactants[a]				
A	3.1–2.4	3.4–3.8	3.6–2.7	6.1–4.2
B	3.0–2.0	3.4–3.1	3.4–2.5	5.4–4.6
F	3.8–2.0	3.8–2.8	3.9–3.4	4.6–5.4
H	2.7–2.2	3.5–2.7	2.7–4.2	4.3–3.9
Av.	3.2–2.2	3.5–3.0	3.4–3.2	5.1–4.5
Nonionic surfactants[a]				
C	4.1–1.5	2.4–0.0[b]	3.4–1.0	6.1–6.1
D	4.2–2.2	3.8–2.4	3.8–3.8	6.8–6.8
E	3.4–1.3	3.1–0.8	2.7–2.0	5.4–3.9
G	2.5–2.2	2.3–0.0[b]	6.8–1.7	5.4–3.9
Av.	3.6–1.8	2.9–0.8	4.2–2.1	5.9–5.2

[a] Additions of 0.25 and 1.25 pounds of surfactant per ton of superphosphate.
[b] Products crumbled and fell from can before hardness could be measured.