Effect of Surface-Active Agents on Preparation of Normal Superphosphate

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The effect of anionic and nonionic surface-active agents on the chemical reactions involved in the manufacture of normal superphosphate was studied to establish whether specific benefits could be derived from their use. Within the limits of concentration studied, the surface-active agents increased the rate and degree of conversion of unavailable phosphorus pentoxide to the available forms. Compared on an equivalent available phosphorus pentoxide basis, the free-acid content of the surfactant-contained superphosphate was always greater than the control. The fluorine loss during acidulation of the phosphate rock was not affected by the presence of surface-active agents.

THE USE OF SURFACE-ACTIVE AGENTS in the production of superphosphate and mixed-goods fertilizers has become increasingly popular with many manufacturers (*1*, *6–8*), but there has been considerable controversy concerning the specific benefits attainable from their use (*1*, *6*). The authors believe that much of the controversy has arisen from the fact that different observers (particularly plant observers) in looking for one particular effect have overlooked many of the attendant effects and, therefore, have reached erroneous conclusions concerning the over-all efficacy of these materials.

In order to aid both the laboratory and plant observers, a general classification of the many effects which have been reported to the authors is presented. Although specific items are listed under each of the main categories, there may be some overlapping between the various categories.

Category A

Effects Concerned with Mechanics of Processing (*6–8*)

1. Cleanliness of processing and conveying equipment
2. Capacity of grinding and bagging equipment
3. Load on dust-collecting equipment
4. Capacity of superphosphate den
5. Over-all rate of production

Category B

Effect on Physical Properties of Intermediate and Finished Products (*1*, *4*, *6–8*)

1. Physical nature of superphosphate while in den
2. Dusting properties of finished goods
3. Tendency of products to cake during curing pile storage and bag storage
4. Amount of solid conditioning agents required in mixed-goods fertilizers

Category C

Effects on Chemical Reactions and Chemical Properties (*4*, *6–8*)

A. Superphosphate
   1. Moisture content
   2. Free-acid content
   3. Fluorine content
   4. Rate and degree of conversion of unavailable P_2O_5 to available forms
   5. Temperatures attained during acidulation

B. Mixed-goods fertilizers
   1. Moisture content
   2. Reversion on ammoniation
   3. Efficiency of ammoniation (rate and degree)
   4. Temperatures attained during ammoniation

The classification clearly illustrates that there may be numerous effects attendant on the use of surface-active agents in fertilizer manufacture. Unless both the laboratory and plant experiences are definitively reported, misunderstanding, confusion, and much unnecessary controversy can readily result.

The laboratory studies reported here deal with some of the effects listed under Category C. Specifically, these studies are concerned with the effect of surface-active agents, both anionic and nonionic, on the free-acid content, fluorine content, and the rate and degree of conversion of phosphorus pentoxide during the preparation of normal superphosphate.

Materials

The chemical and screen analyses for the milled Florida land pebble phosphate rock used in all of the experiments are given in Table I. The screen analyses are the range of values obtained from several determinations using a Tyler Ro-Tap instrument.

Sulfuric acid (55° Baumé, 60.9%) was employed as the acidulating agent. It was prepared by diluting reagent grade concentrated sulfuric acid (95.96%) and was standardized by acidimetric titration.

Two types of surface-active agents, anionic and nonionic, were evaluated (Table II).

Experimental Procedure

The acidulations of the phosphate rock were carried out with a Kitchen-Aid mixer which was equipped with an 8-inch stainless steel bowl and a constant-

Table I. Chemical and Screen Analyses of Florida Land Pebble Phosphate Rock

Chemical Analysis: Constituent	%	Screen Analysis: Screen mesh	%
Total P_2O_5	35.26	+60	0
Available P_2O_5	5.64	−60, +100	5–10
CaO	49.02	−100, +200	25–30
BPL	77.0	−200	60–65
SiO_2	3.48		
CO_2	2.61		
F	3.26		
Moisture (105° C.)	0.61		

Table II. Description of Surface-Active Agents

Surface-Active Agent	Type	Physical State	Composition: Active	Composition: Inert
Santomerse No. 1[a]	Anionic	Solid	40% sodium salt dodecyl benzene sulfonic acid	60% sodium sulfate
Santomerse E[a]	Anionic	Solid	75% sodium salt C_5-C_6 benzene sulfonic acid	25% sodium sulfate
Sterox AJ-100[a]	Nonionic	Liquid	100% ethylene oxide–higher alcohol condensate	...

[a] Trade name, Monsanto Chemical Co.

Table III. Solubility of Surface-Active Agents in 55° Bé. Sulfuric Acid at 125° F.

(Use concentrations of surface-active agents in sulfuric acid and in finished product on an active and total basis)

Surface-Active Agent	Solubility in 55° Bé. H_2SO_4 at 125° F., %	G. Used per 1750 G. Rock, 1538-G. Acid Charge	Concn. on Active Basis, %: In acid	Concn. on Active Basis, %: In finished product	Concn. in Finished Product, Lb./Ton: Active basis	Concn. in Finished Product, Lb./Ton: Total basis
Santomerse No. 1	0.05	0.82	0.021	0.01	0.2	0.5
		1.64	0.043	0.02	0.4	1.0
		3.28	0.086	0.04	0.8	2.0
Santomerse E	0.05	0.44	0.021	0.01	0.2	0.27
		0.88	0.043	0.02	0.4	0.53
		1.76	0.086	0.04	0.8	1.07
Sterox AJ-100	Miscible in all proportions	0.33	0.021	0.01	0.2	0.2
		0.66	0.043	0.02	0.4	0.4
		1.32	0.086	0.04	0.8	0.8

speed (60 r.p.m.) eccentrically rotating stainless steel blade.

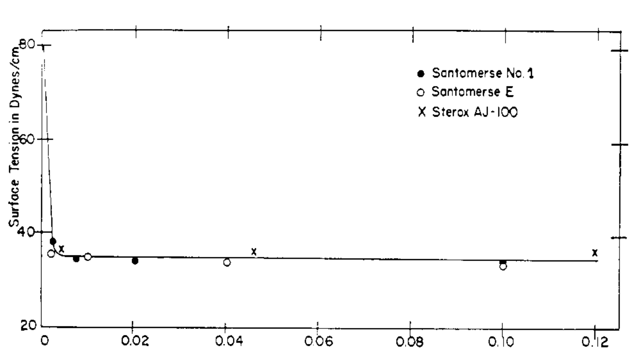
In all experiments, 1750 ± 0.5 grams of milled phosphate rock was introduced into the mixing bowl, agitation started, and 1538 ± 0.5 grams of hot (120° to 125° F.) 55° Bé. sulfuric acid added over a period of 10 to 15 seconds. This corresponds to 1.58 pounds of 100% sulfuric acid per pound of phosphorus pentoxide. The reacting system was allowed to mix for 1 minute and then transferred to a fiber drum (0.5-gallon capacity) in which it was allowed to den for 30 minutes. In all cases, the product was in a sufficiently solid state at the end of the mixing period to permit transfer. Temperature measurements were made while the product was still in the mixing bowl, just prior to transfer to the den.

The superphosphate was removed from the den, passed through a 6-mesh screen, and sampled for a zero time sample (ca. 300 grams), and the remainder was distributed evenly between ten 16-ounce glass jars. The jars were sealed, using vacuum tape, and stored in a constant temperature oven held at 165° to 175° F. It was assumed that curing under these conditions would more closely correspond to actual plant storage than curing in open containers, where nearly all of the moisture would be lost. The system of sealing was not completely satisfactory, however, in that some of the samples showed considerable moisture loss.

The surface-active agents were introduced into the reaction system by dissolving or suspending them in the hot sulfuric acid. Of the three materials evaluated, only Sterox AJ-100 was completely soluble at all concentrations used. Both the Santomerse No. 1 and the Santomerse E were soluble at concentrations below 1 part of surface-active agent (on an active basis) in 5000 parts of acid. At higher concentrations the excess surfactant was uniformly suspended throughout the acid in the form of finely divided oily droplets. This dispersion was achieved by vigorous agitation of the acid prior to its introduction onto the phosphate rock.

Three concentrations of surface-active agents were employed—0.01, 0.02, and 0.04%. In all cases, the concentration value is based on the percentage of active surfactant in the finished superphosphate. Table III gives the amounts of the various surface-active agents used, their solubility in 55° Bé. sulfuric acid, and their concentration in the acid and in the final product.

Figure 1. Effect of surface-active agents on surface tension of 55 Bé. sulfuric acid at 90° F.



Samples of the superphosphate were removed periodically from the oven over an interval of 25 days and analyzed by standard methods for total phosphorus pentoxide (*2*), ammonium citrate-insoluble (*2*), free-acid content (*5*), and moisture content (*2*). The citrate-soluble phosphorus pentoxide values were determined by difference between the total phosphorus pentoxide and citrate-insoluble phosphorus pentoxide values.

Fluorine was determined only on the original phosphate rock and in the zero time samples by the standard distillation technique followed by titration with thorium nitrate (*2*). The fluorine loss was determined by comparison of the mole ratio of fluorine to phosphorus pentoxide (F/P_2O_5) of the original rock with that of the zero time samples.

All surface tension measurements were made using a du Noüy tensiometer.

Effect of Surface-Active Agents

Effect on Surface Tension of Sulfuric Acid. As a preliminary indication of the suitability of the surface-active agents in the acidulation of phosphate rock, their effect on the surface tension of 55° Baumé sulfuric acid was measured at 90° F. The results are shown in Figure 1. It is clear that the surface tension lowering brought about by these three surfactants is approximately the same in each case and that the amount of each surfactant required to lower the surface tension to a minimum value is extremely small—about 0.0025%. As the surfactants evaluated differ from one another in their effectiveness in phosphate

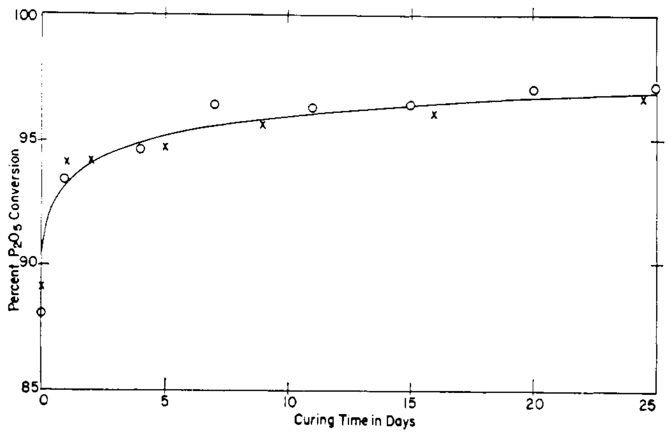


Figure 2. Per cent phosphorus pentoxide conversion as a function of time in absence of surface-active agents

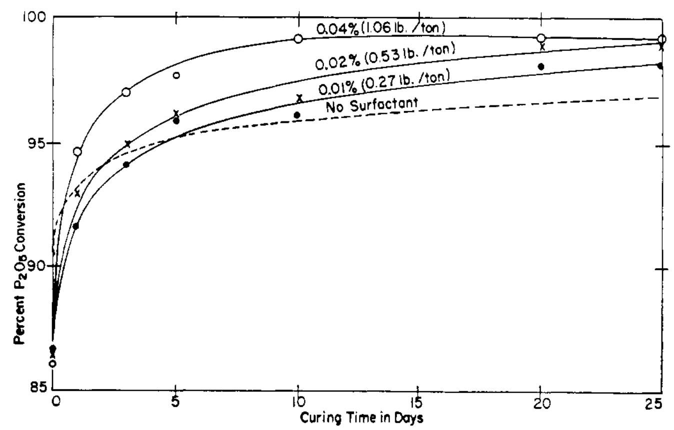


Figure 3. Effect of Santomerse E on degree and rate of curing of normal superphosphate

rock acidulation, it may be concluded that the effect on the surface tension of sulfuric acid cannot be used as an evaluatory tool. Probably such factors as stability in the reaction system, steam volatility, solubility of metal ion salts, and rate of wetting govern the effectiveness of surface-active agents as acidulation aids.

Effect on Rate and Degree of Curing of Normal Superphosphate. The data concerning the rate and degree of curing of normal superphosphate without surface-active agent (control) are plotted in Figure 2. This curve was established from the data obtained from several different acidulations. The actual points plotted are from the two experiments which gave the most widely divergent results. The phosphorus pentoxide conversion levels off after about 7 days' curing time at 96.4% and reaches a maximum of 97.0% in 25 days.

Figures 3, 4, and 5 show the effect of three concentrations of the three surface-active agents on the rate and degree of curing of the normal superphosphate. The superimposed dotted curve represents the curing curve for the normal superphosphate prepared in the absence of surface-active agents (control).

In each case where surfactant was used in the acidulation, the rate and degree of curing were in excess of that obtained from the control sample. Samples containing 0.01, 0.02, and 0.04% of Santomerse E showed 25-day conversion of 98.1, 99.0, and 99.2%, respectively, as compared to 97.0% for the control sample (Figure 3). The rate of curing was increased by the presence of Santomerse E, in that samples containing 0.01, 0.02, and 0.04% of the surfactant reached 97.0% conversion, the value for the fully cured control, after 13, 8, and 3 days, respectively. With Santomerse No. 1, the degree of conversion of the phosphorus pentoxide to the nutritionally available forms was less than that obtained with Santomerse E but was in excess of the 97.0% conversion obtained with the control (Figure 4). The 25-day values for 0.01, 0.02, and 0.04% Santomerse No. 1 were 97.6, 97.9, and 97.7%, respectively. The rate of conversion was again increased, in that the value of 97.0% conversion was attained after about 5 to 6 days for all three concentrations of Santomerse No. 1. With both Santomerse E and Santomerse No. 1, there was an initial inhibitory effect on the rate of conversion which was not exhibited by the nonionic surfactant.

The conversion values obtained using Sterox AJ-100 were similar to Santomerse No. 1 and less effective than Santomerse E. Conversion values for 0.01, 0.02, and 0.04% surfactant after 25 days were 97.9, 98.0, 98.0%, respectively. The rate of conversion was again increased as the 25-day 97.0% conversion (Figure 5) of the control was surpassed after 8, 5, and 4 days for the 0.01, 0.02, and 0.04% concentrations, respectively, of Sterox AJ-100.

In all cases where surface-active agents were used, their effect on the rate and degree of phosphorus pentoxide conversion had not become clearly apparent in the first 24 hours of curing. This is in agreement with results reported by other investigators (*4*).

Effect on Free-Acid Content of Normal Superphosphate. The data as presented in Tables IV and V best show the effect of the surface-active agents on the free-acid content of normal superphosphate. Normal superphosphate prepared in the presence of the surface-active agents and cured for 25 days in most cases shows slightly less free acid than do the control samples. This reduction in the 25-day free-acid content can best be explained by the fact that the greater total phosphorus pentoxide conversion in the presence of surface-active

Figure 4. Effect of Santomerse No. 1 on degree and rate of curing of normal superphosphate

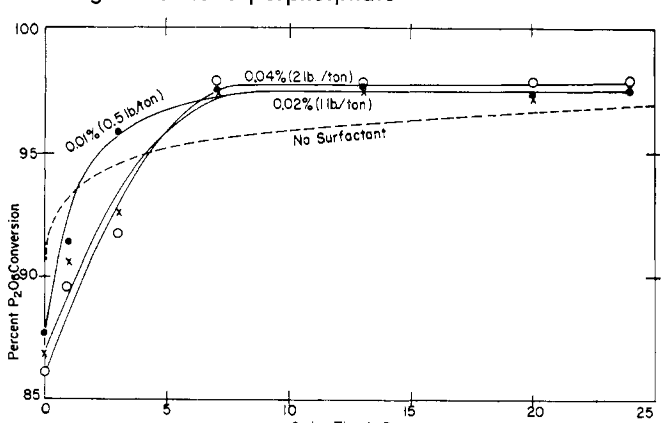


Figure 5. Effect of Sterox AJ-100 on degree and rate of curing of normal superphosphate

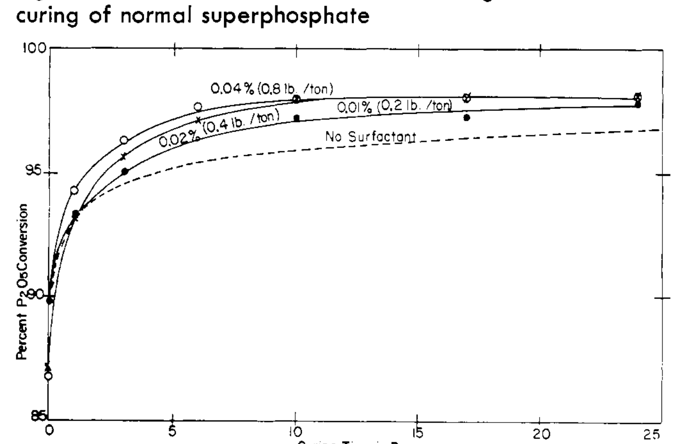


Table IV. Effect of Concentration of Surfactant and Curing Time

(On free acid content and availability of P_2O_5 in normal superphosphate)

Surfactant	Concn., %	Max. Temp., during Acidulation, ° F.	Curing Time, Days	Composition, %				
				Moisture	Free acid (H_2SO_4)	Total P_2O_5	Citrate-ins. P_2O_5	Conversion
None	0.00	230	0	11.33	6.24	20.08	2.51	87.5
			1	10.58	4.29	20.85	1.38	93.4
			4	9.99	3.21	20.99	1.12	94.7
			7	10.25	3.00	21.17	0.75	96.4
			11	8.78	2.67	21.27	0.78	96.3
			15	9.22	2.46	21.17	0.76	96.5
			21	8.07	2.13	21.65	0.64	97.0
			25	9.08	2.28	21.41	0.63	97.1
None	0.00	232	0	11.33	4.94	20.27	2.22	89.0
			1	10.26	3.78	21.21	1.20	94.3
			4	10.96	3.64	21.00	1.18	94.4
			5	10.27	3.38	21.45	1.09	94.9
			9	10.67	3.17	21.11	1.09	95.7
			16	8.99	2.32	21.51	0.84	96.1
			24	8.62	2.16	22.82	0.70	96.9
Santomerse E	0.01	230	0	11.64	5.72	20.84	2.74	86.8
			1	10.97	4.26	21.04	1.73	91.8
			3	9.80	3.28	21.31	1.23	94.2
			5	9.92	3.03	22.34	0.84	96.2
			10	9.37	2.68	21.42	0.82	96.2
			20	3.80	1.72	22.73	0.43	98.1
			25	3.85	1.78	22.20	0.42	98.1
Santomerse E	0.02	236	0	11.74	6.52	19.95	2.77	86.1
			1	11.08	4.39	20.46	1.45	92.9
			3	9.99	3.52	20.71	1.05	94.9
			5	9.75	3.05	20.77	0.81	96.1
			10	9.27	2.84	21.09	0.67	96.8
			20	7.03	2.14	21.39	0.25	98.8
			25	8.42	1.66	21.43	0.21	99.0
	0.04	235	0	12.21	7.04	20.23	2.82	86.1
			1	11.51	4.54	20.41	1.09	94.7
			3	10.35	3.91	20.68	0.60	97.1
			5	10.98	3.53	20.60	0.47	97.7
			10	7.69	2.94	21.30	0.15	99.3
			20	9.96	1.66	20.77	0.16	99.2
			25	8.34	1.46	21.10	0.17	99.2
Santomerse No. 1	0.01	230	0	11.14	5.05	19.44	2.32	88.1
			1	9.32	4.20	19.60	1.68	91.4
			3	10.20	3.74	19.42	0.81	95.8
			7	4.90	3.04	20.34	0.45	97.8
			13	8.28	2.20	21.33	0.50	97.6
			20	8.56	2.33	21.27	0.56	97.4
			24	8.42	1.98	21.26	0.50	97.6
	0.02	230	0	10.94	4.85	21.32	2.61	87.7
			1	11.35	4.14	20.30	1.86	90.8
			3	11.17	3.98	20.34	1.46	92.8
			7	9.09	3.14	20.82	0.50	97.6
			13	9.37	2.55	20.75	0.47	97.7
			20	1.60	2.37	22.10	0.61	97.2
			24	6.96	2.27	20.65	0.43	97.9
	0.04	238	0	10.97	4.64	20.56	2.75	86.6
			1	10.96	4.29	20.14	2.08	89.7
			3	11.28	4.08	19.78	1.62	91.8
			7	5.43	2.75	21.39	0.47	97.8
			13	6.38	2.28	21.18	0.45	97.9
			20	1.19	1.53	22.01	0.48	97.8
			24	1.26	1.68	22.00	0.50	97.7
Sterox AJ-100	0.01	228	0	11.98	4.72	20.11	2.15	89.3
			1	10.02	3.50	20.87	1.44	93.1
			3	11.11	3.20	20.74	1.00	95.2
			6	10.54	3.29	20.75	0.98	95.3
			10	8.64	2.52	21.19	0.60	97.2
			17	10.00	2.40	21.00	0.52	97.5
			24	8.17	2.39	21.47	0.45	97.9
	0.02	230	0	12.55	4.70	20.44	2.69	86.8
			1	10.43	3.70	20.97	1.45	93.1
			3	11.12	3.16	20.26	0.92	95.5
			6	9.72	2.93	21.13	0.59	97.2
			10	6.50	2.47	21.89	0.46	97.9
			17	2.00	2.01	23.62	0.74	96.9
			24	1.80	1.97	22.94	0.45	98.0
	0.04	236	0	12.70	5.97	20.08	2.82	86.0
			1	10.65	3.77	20.86	1.25	94.0
			3	11.04	3.05	21.35	1.05	95.2
			6	9.71	3.19	21.08	0.51	97.6
			10	10.08	2.61	21.00	0.45	97.9
			17	9.38	2.39	20.66	0.45	97.9
			24	8.05	2.08	22.41	0.45	98.0

agents consumes more of the available acid.

However, the free-acid content of the superphosphate samples prepared with surface-active agents and cured to an available phosphorus pentoxide comparable to that of the fully cured control was always greater than that of the control. This can be interpreted to mean that the presence of surface-active agents in the acidulation process increases the effectiveness of the acid, and hence in order to achieve a given degree of conversion, less sulfuric acid would be required.

Effect on Loss of Volatile Fluorides during Acidulation. The analytical data showing the effect of the surface-active agents on the loss of fluorine during the acidulation of phosphate rock are summarized in Table VI. They show that the loss of fluorine as volatile fluorides was not affected by any of the surface-active agents. The fluorine loss from the control samples was 24.4 and 16.6%, while in the presence of the surfactants the loss ranged from 19.0 to 27.5%. These values are in good agreement with the results of other investigators, who report that usually 25 to 30% of the fluorine content of the phosphate rock is evolved in acidulation (*3*).

Table V. Effect of Surface-Active Agents on Free Acid Content of Normal Superphosphate as Function of Degree of Conversion

Surfactant	Concn., %	P_2O_5 Conversion, %	Days of Curing	Free Acid Content, %
No surfactant		97.0	21	2.13
		97.1	25	2.28
		96.9	24	2.16
Santomerse E	0.01	98.1	20	1.72
	0.01	98.1	25	1.78
	0.02	96.8	10	2.84
	0.02	99.0	25	1.66
	0.04	97.1	3	3.91
	0.04	99.2	25	1.46
Santomerse No. 1	0.01	97.8	7	3.04
	0.01	97.6	24	1.98
	0.02	97.6	7	3.14
	0.02	97.9	24	2.27
	0.04	97.8	7	2.75
	0.04	97.7	24	1.68
Sterox AJ-100	0.01	97.2	10	2.52
	0.01	97.9	24	2.39
	0.02	97.2	6	2.93
	0.02	98.0	24	1.97
	0.04	97.6	6	3.19
	0.04	98.0	24	2.08

Conclusions

The conclusions set forth are based solely on the experimental work presented in this communication.

The effect of surface-active agents on the surface tension of 55° Bé. sulfuric acid cannot be used as a preliminary screening method for predicting the relative effectiveness of different surfactants on the acidulation of phosphate rock.

The use of surface-active agents in phosphate rock acidulation increases both the rate and degree of phosphorus pentoxide conversion.

Within the limits of 0.01 to 0.04% active concentration, the effect of the surface-active agents on the rate and degree of phosphorus pentoxide conversion is proportional to amount used.

The anionic type of surfactant has a slight inhibitory effect during the initial curing period. This effect is not exhibited by the nonionic type.

The free-acid content of the normal superphosphate prepared in the presence of the surface-active agents and cured for 25 days is slightly lower than that of the normal superphosphate prepared in the absence of surface-active materials.

The free-acid content of the normal superphosphate containing surface-active agent and cured to an available phosphorus pentoxide content comparable to that of the fully cured control is greater than that of the control.

The loss of fluorine as volatile fluorides during the acidulation of phosphate rock is not affected by the presence of surface-active agents.

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Received for review November 1, 1954. Accepted December 17, 1954. Presented in part before the Division of Fertilizer and Soil Chemistry, Symposium on Fertilizer Technology, at the 124th Meeting, American Chemical Society, *Chicago, Ill., 1953.*

Table VI. Effect of Surface-Active Agents on Loss of Volatile Fluorides

Material	Composition, % Surfactant	Composition, % Surfactant Concn.	Composition, % Fluorine	Composition, % P_2O_5	F/P_2O_5 Mole Ratio	Fluorine Lost, %
Phosphate rock	...	...	3.26	35.26	0.695	...
Superphosphate[a]	None	0.000	1.41	20.06	0.526	24.4
	None	0.000	1.58	20.27	0.580	16.6
	Santomerse E	0.01	1.46	20.84	0.515	25.9
		0.02	1.39	19.95	0.522	24.9
		0.04	1.36	20.23	0.504	27.5
	Santomerse No. 1	0.01	1.36	19.44	0.522	24.9
		0.02	1.49	21.32	0.523	24.8
		0.04	1.55	20.56	0.563	19.0
	Sterox AJ-100	0.01	1.50	20.11	0.560	19.4
		0.02	1.46	20.44	0.534	23.2
		0.04	1.52	20.08	0.563	19.0

[a] Fluorine determinations made on zero time samples only.