In analyzing the crop results obtained, the following facts are noted:

Acid phosphate has returned a crop increase over 6 times as profitable per acre as has raw rock phosphate. Acid phosphate has returned a crop increase over 7 times as profitable per dollar invested as has raw rock phosphate.

Each pound of phosphorus in acid phosphate has returned a crop increase valued at $28\frac{1}{3}$ cents. Each pound of phosphorus in raw rock phosphate has returned a crop increase valued at $3\frac{1}{2}$ cents. A pound of phosphorus in acid phosphate has returned a crop increase over 8 times as valuable as that returned by a pound of phosphorus in raw rock phosphate.

By taking the prices used in this paper for farm crops, the increases obtained by the application of phosphates would give a value of \$38.85 per ton for acid phosphate and \$8.40 per ton for raw rock phosphate. If the prices for farm products were reduced 20 per cent. the acid phosphate would have a value of \$31.08 per ton and the raw rock phosphate a value of \$6.72 per ton. The acid phosphate would still show a good profit and the raw rock phosphate would be used at a loss.

By calculating the phosphoric acid in all the crops grown, it is found that 224 lbs. of P_2O_5 have been recovered in the total increase caused by acid phosphate and 147 lbs. of P_2O_5 have been recovered in the total increase caused by raw rock phosphate. These amounts of P_2O_5 are approximately $\frac{1}{12}$ of the phosphoric acid applied in the acid phosphate and $\frac{1}{85}$ of the phosphoric acid applied in the raw rock phosphate.

Nineteen samples of raw rock phosphate were taken on the Indiana market in 1915 by the inspectors of the State Chemist. The analyses of these samples show an average of 28.8 per cent total P_2O_5 and an average of 1.8 per cent ammonium citrate-soluble P_2O_5 ; 1.8 per cent of all the raw rock phosphate used in the 82 tests would indicate an available phosphoric acid amount of 804 lbs. or over 5 times as much as was removed by the increased crops caused by the raw rock phosphate in $3\frac{1}{2}$ years.

On the Scottsburg field,¹ which has been running for 10 yrs., raw rock phosphate came the nearest to paying as large a profit as acid phosphate, the net returns per acre for the 10-yr. period being \$31.52 for the acid phosphate and \$19.51 for the raw rock phosphate. On the Scottsburg field, 88 lbs. per acre of citrate-soluble P_2O_5 were added in acid phosphate in 10 yrs. and 26 lbs. of P_2O_5 were removed in the increased crops. If 1.8 per cent is considered the measure of the citrate-soluble phosphate in the rock phosphate used, then 72 lbs. of citrate-soluble phosphate were added per acre in raw rock phosphate in 10 yrs. while 26 lbs. of P_2O_5 were removed in the increased crops.

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¹ See *Indiana Bull.* 187, 1064.

THE ACTION OF CALCIUM CARBONATE ON ACID PHOSPHATE¹

By EOBERT W. MAGRUDER

The reaction which takes place between calcium carbonate and acid phosphate is one of great interest both to the farmer and to the fertilizer manufacturer. It has been generally taught that calcium carbonate should not be mixed with acid phosphate because it would act on the mono- and di-calcium phosphates and convert them into the tri-calcium phosphate, which is insoluble in water and slowly available to plants. Consequently to find that Mr. J. S. Burgest, State Agronomist of North Carolina, in *Bulletin* 220 of the North Carolina Department of Agriculture, recommended that ground limestone and acid phosphate be mixed in the proportions of 1200 lbs. of the former to from 400 to 1000 lbs. of the latter, was very much of a shock to me.

Mr. Burgest says: "No attempt has been made to leave the impression that acid phosphate mixed with ground limestone will not revert to what is called di-calcium and, to some extent, to tri-calcium forms. But these forms of phosphorus are still available to the crops, while the iron and aluminum phosphates are entirely out of reach of the plants."

To how great an extent acid phosphate is converted into iron or aluminum phosphates in the soil I do not know, but in the Eastern and Southern states experimental results have uniformly shown that acid phosphate gives much better results and is more profitable than ground phosphate rock. Di-calcium phosphate is, of course, a valuable fertilizer, and tri-calcium phosphate which has been formed by the reversion of acid phosphate would, without doubt, be more available to plants than ground phosphate rock on account of its fine subdivision.

If reverted phosphate is better for crops than acid phosphate, the fertilizer laws all need amending and the manufacturers of acid phosphate need to change their methods of manufacture. They should put out no mono-calcium phosphate, but only di- and tri-calcium phosphates.

The only recent experiments on the reaction between limestone and acid phosphate I have seen are those of Dr. R. N. Brackett,² of Clemson College, South Carolina. His limestone contained only a trace of phosphoric acid, and his acid phosphate was of the following composition:

Total phosphoric acid.....	16.84
Water-soluble phosphoric acid.....	13.55
Insoluble phosphoric acid.....	1.33

The following mixtures were used and results obtained:

No.:	1	2	3	4
Lbs. acid phosphate.....	14.0	15.5	17.0	10.0
Lbs. ground limestone.....	6.0	4.5	3.0	10.0

¹ Presented at 53rd Meeting of American Chemical Society, New York City, September 25 to 30, 1916.

² *THIS JOURNAL*, 7 (1915), 620.

PERCENTAGE ANALYSES OF MIXTURES

Mixture	No. 1		No. 2		No. 3		No. 4	
	W-S	Ins.	W-S	Ins.	W-S	Ins.	W-S	Ins.
April 21st, Immediately after mixing...	6.15	1.07	8.30	1.15	10.50	1.24	2.40	0.83
May 10th.....	3.05	1.30	3.84	1.26	8.66	1.37	0.99	0.98
June 12th.....	3.31	1.39	6.39	1.66	8.15	1.59	1.10	1.11
Sept. 13th.....	3.38	1.46	3.31(a)	1.33	8.05	1.46	0.87	1.08

(a) This is probably an error as an analysis in November, 1913, gave about five per cent water-soluble.

I was surprised that more insoluble phosphate was not formed in these mixtures, especially the half and half mixture.

In order to test the effect of larger mixtures than used by Dr. Brackett and also to try the effect of fresher acid phosphate, I made up some mixtures last summer and used acid phosphate a month old and some which had been made only a few days and was warm when mixed. I used ground oyster shells instead of ground limestone.

TABLE I—MATERIALS USED

Material	Percentages Phosphoric Acid	
	Total	Insoluble Water-Soluble
New acid phosphate.....	19.33	2.41 15.78
Month-old acid phosphate.....	18.13	1.04 14.80
Ground oyster shells.....	0.51	.....

TABLE II—MIXTURES AND RESULTS OF ANALYSES

Acid Phosphate Used:		OLD		NEW	
MIXTURE	Date Analyzed	Phosphoric Acid (%) Insol.	Water-Sol.	Phosphoric Acid (%) Insol.	Water-Sol.
190 lbs. Acid Phos....	8/16	2.50	15.05	0.82	13.72
10 lbs. Oyster Shells..	9/20	2.70	14.00	0.24	11.28
	Theory	2.32	14.99	1.02	14.06
180 lbs. Acid Phos....	8/16	2.45	14.50	0.79	13.38
20 lbs. Oyster Shells..	9/20	3.44	7.08	1.50	3.05
	Theory	2.22	14.20	0.99	13.32
160 lbs. Acid Phos....	8/16	2.40	12.15	0.84	11.10
40 lbs. Oyster Shells..	9/20	2.99	4.30	1.57	1.05
	Theory	2.03	12.62	0.93	11.84
140 lbs. Acid Phos....	8/16	1.65	10.08	1.14	10.58
60 lbs. Oyster Shells..	9/20	3.26	1.50	1.95	0.65
	Theory	1.84	11.05	0.89	10.36
100 lbs. Acid Phos....	8/16	1.95	5.55	1.12	7.60
100 lbs. Oyster Shells	9/20	2.32	0.30	1.11	0.35
	Theory	1.46	7.89	0.77	7.40

In studying this table there are some inconsistencies, but taking the results as a whole it is seen:

- 1—That the new acid phosphate is acted on more readily by the oyster shells than the older.
- 2—That action begins at once.
- 3—That the action continues on standing.
- 4—That the greater the amount of oyster shells the greater the action.
- 5—That with 30 and 50 per cent shells virtually all of the water-soluble phosphoric acid disappears.

These results, on the whole, agree with Dr. Brackett's. I intend to make further analyses of these samples.

It has generally been considered that water-soluble or mono-calcium phosphate is more valuable to crops than citrate-soluble, or di-calcium phosphate. If that is true then mixing larger quantities of calcium carbonate with acid phosphate would reduce the value of the phosphate very greatly, by reducing the water-soluble phosphoric acid to the vanishing point and also by increasing the insoluble phosphoric acid.

As the fertilizer laws are at present, fertilizer manufacturers certainly could not afford to mix much calcium carbonate with their acid phosphates on account of the high insoluble phosphoric acid which would be produced.

As this question is a very important one to both farmers and fertilizer manufacturers, I have thought it well to make public my results in order to have more light thrown on the subject.

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A CONTRIBUTION TO THE THEORY OF EMULSIFICATION BASED ON PHARMACEUTICAL PRACTICE¹

By LEO ROON AND RALPH E. OESPER

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INTRODUCTORY

The practical knowledge of emulsions, which has been handed down to the pharmacists from generation to generation, has been surveyed by physical chemists, but this pharmaceutical experience has been neglected almost entirely as an aid in developing a rational theory of emulsification. Several theories of emulsification have been proposed which differ according to the factor held responsible for the stability of the emulsion, but objection has been raised to all of them. It is probable that none of these theories is of universal application, and though each may cover special cases or classes of emulsions, their inadequacy is generally admitted.

The surface tension theory upheld by Plateau,² Quincke³ and notably Donnan⁴ was shown to be inadequate when Pickering⁵ emulsified "solar distillate" with the aid of such materials as the basic sulfates of iron and copper, hydrous ferric oxide, etc., materials which do not influence surface tension. The viscosity theory, whose origin is obscure, was attacked by Hillyer,⁶ who pointed out that although extreme viscosity was an important factor in the preparation of some pharmaceutical emulsions, nevertheless, viscous materials, such as 50 per cent glycerine or 6 per cent gum solution, are not able to emulsify kerosene or cottonseed oil, though dilute, comparatively mobile soap solutions do so easily.

While admitting the favorable influences of high viscosity and low surface tension, Pickering⁷ put forth the view that the deciding factor is the formation of films of insoluble particles around the droplets. Donnan⁸ attacked this hypothesis bitterly, but Bancroft⁹ pointed out that the criticism was beside the point and that the theory was not intended to be a complete one. Clowes¹⁰ has described experiments in which these films were distinctly visible and he attributes their action in part to a purely mechanical action in keeping the particles from coalescing, in part to lowering of surface tension and in part to repulsive action of the electrically charged particles.

Fischer¹¹ has recently proposed that emulsification is due to, or accompanied by, the formation of a hydration colloid compound. He says: "In reviewing the empirical instructions for the preparation of emulsions, and in our own attempts to formulate such as would always yield permanent results, we were struck with the fact that their production is always associated

¹ The work reported in this article constitutes the basis of a thesis submitted by Leo Roon to the Faculty of the Graduate School of New York University, in part fulfillment of the requirements for the degree of Master of Science.

² *Pogg. Ann.*, **14** (1870), 44.

³ *Wied. Ann.*, **35** (1888), 589.

⁴ *Z. phys. Chem.*, **31** (1899), 42.

⁵ *J. Chem. Soc.*, **91** (1907), 200.

⁶ *J. Am. Chem. Soc.*, **25** (1903), 513.

⁷ *Z. Koll. Chem.*, **7** (1910), 11.

⁸ *Ibid.*, **7** (1910), 214.

⁹ *J. Phys. Chem.*, **16** (1912), 504.

¹⁰ *Ibid.*, **20** (1916), 415.

¹¹ *Science*, **43** (1916), 468.