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Studies on the manufacture of
non-retrograding superphosphate and
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By

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Chapter 1.

Introduction.

The physiological effects of phosphoric acid upon plants are stated as follows, namely as a structural material of the plant body, unstable phosphates concerning the metabolism of carbohydrates and fats, phosphatid phosphoric acid for the construction of the cell, the cell nucleus forming phosphoric acid in the form of nucleoprotein and other, buffer phosphoric acid in cell saps and tissue saps which regulate their hydrogen ion concentration. Concerning the nucleus formation, phosphoric acid is said to be necessary for reproduction.

The superphosphate is generally accepted as the most important source of phosphoric acid, and it is seen as an important manure in company with ammonium sulphate and potassium sulphate. Therefore, studies regarding the increasing of the effects of superphosphate are the most principal, which should not be disregarded. However, studies on the manufacture and the properties of superphosphate regard mostly the increasing of the efficiency of its manufacture or chemical changes between soil components and superphosphate when it is supplied to the soil, the affirmation of its retrograding to insoluble form during its storage, and the statement of its small efficiency as a manure.

The importance of superphosphate as a manure is due to the water-solubility of its phosphate in the same way as with other inorganic manures. The other manures such as ammonium sulphate and potassium sulphate retain their solubilities in soil when they are supplied and absorbed by soil components and are utilized by plants. When superphosphate is supplied to soil, its main component, monocalcium phosphate distributes widely throughout soil components owing to its solubility, and is absorbed and retained by soil. However, it reacts with soil components, changes to bicalcium and tricalcium phosphates when the calcium content of the soil is not small, changes to iron phosphate and aluminium

phosphate in acid soil, thus it decreases its solubility gradually. Mono-calcium phosphate is absorbed and utilized at once by plant roots, bicalcium phosphate is absorbed and utilized when it is dissolved by juice excreted from plant roots, the other insoluble phosphates are absorbed and utilized when they are dissolved and dispersed by carbonic acid of rain water or of underground water or by humic acids of soil. According to these special properties of superphosphate, it is said to be a less efficient manure than the other soluble inorganic manures. Therefore, it is especially necessary to devise and improve the methods of its manuring technique.

Concerning the settlement of these problem, the following results have been reported. Van Bemmelen (1) stated that, when an ammoniacal or alkaline solution of humus substances was added to soil, not only tolerable quantities of silicic acid, iron oxide, alumina and alkaline earths, but also phosphoric acid dissolved into this alkaline humus solution. Accordingly, an abundant quantity of phosphoric acid was found in soil solution. He found further that not only humus substances but also proteins, glycerine, sugars, bases and salts had the same action.

Mack (2) believed in the same way as van Bemmelen. He observed the formation of a loose humate-phosphoric acid-complex. Especially owing to the existence of free OH ion, he believed in the formation of a soluble humophosphate-iron-complex and of a humophosphate-aluminium-complex.

Spencer and Stewart (3) divided the plant nutrients into two sorts, i.e. the chemically available and the positionally available nutrients. The former were in such a chemical form that when coming in contact with plant roots, they were at once assimilated. The latter located in soil where plant roots were able to come in contact with them. When a soluble phosphate was supplied to soil, on account of its water-solubility, it resulted in an entirely satisfactory distribution of the nutrient throughout the soil and its positional availability was increased. According to their experiments, phosphorus in organic phosphates of the type formula $R(OH)_x(OPO_3Mg)_z$ escaped to a marked degree the fixation, and seemed to have a great chemical and positional availability.

Flieg (4) observed, that humate sol hindered the precipitation of soluble phosphoric acid by calcium salts within the all experimental pH-extent (i.e. pH 4.2—8.0); the optimum quantitative relation of humate

to P_2O_5 was one part charcoal as humate to four parts P_2O_5 . In a shaking experiment, humate soil brought remarkable quantities of P_2O_5 into solution not only of soil but also of difficultly soluble raw phosphate. The maximum solubility was observed with one part charcoal as humate to four parts P_2O_5 . The humate effect in soil was mainly by action of anions, but sodium humate showed a specially favorable action. He stated that the phosphate in soil was changed into soluble form and its mobility was markedly increased by humate.

According to Scharrer and Keller (5), when a soluble phosphate fertilizer was supplied to a fruitful soil rich in calcium carbonate, it changed in a short time to calcium phosphate and tricalcium phosphate, thus it diminished its soaking effect into soil. This small mobility was due to the formation of difficultly soluble compounds by the action between phosphoric acid and soil components. This action occurred by the presence of phosphate ion. Therefore, when phosphoric acid was in such a form that it displayed no ionic reaction, the soaking effect into soil of phosphate manure could be retained for a longer period. Many sorts of organic compounds of phosphoric acid were fit for this object. According to their experiments, ester of gluconic acid and phosphoric acid had a remarkable soaking effect. Light soil showed a deeper penetration of organic phosphoric acid compounds than heavy soil. The phosphoric acid was fixed more strongly by acid soil than by neutral soil. The distribution of organic phosphoric acids resulted in the commencement by absorption process, but afterwards by chemical fixation. Then they underwent mineralizing processes, and changed to inorganic compounds. No relation was observed between the mineralizing processes and the pH value of soil. The processes of heavy soil were greater than those of light soils. A close relation was observed between them and the contents of soil colloids. Soil microorganisms consumed the organic components of organic phosphoric acids, accordingly to the promotion of their mineralization.

According to Rautenberg (6), the action of stable manure on soils was a sum of many sorts of physical and chemical processes, but it was difficult to distinguish them separately. Furthermore, the action of microorganisms could not be overlooked. They consumed the residues of plants in soil, rendered them harmless for the next plants, that should grow on the soil. The stable manure improved the physical properties

of soil, heavy soil became looser, the water-capacity was increased with light soil. The phosphoric acid of stable manure was used better than that of artificial manure. These favorable effects of stable manure could have many reasons. One of them was that the stable manure contained organic phosphoric acids which were easily utilized by plants, but hard to be fixed by soil. They might remove cations such as iron and calcium from soil solution which would combine with phosphoric acid to make insoluble phosphate. Furthermore, anions of stable manure might decrease the adsorption of phosphoric acid by soil. The favorable effects of stable manure on the content of phosphoric acid of soil could also be those of physical kind.

The results mentioned above are all of scientific studies performed in experimental laboratories. Practical studies concerning the storage of water-soluble phosphate manure, the prevention of retrogradation to insoluble form in soil, the manufacture of such manures and the practical methods of manuring are very scarce in the present time.

In our country, an increased production of foodstuffs is strongly demanded. Even when phosphoric acid is applied to soil in the most effective form, namely in the form of superphosphate, its efficiency is very small as already stated, the most part of supplied phosphoric acid changing gradually into insoluble form, escaping from the utilization by plants and accumulating in vain in the soil. For the purpose of obtaining the greatest possible yield by the use of a given quantity of material, one must undertake the greatest utilization of phosphoric acid of manure by plants. It need not mention that the studies to prevent the retrogradation of superphosphate to insoluble form which occurs during its storage or in soil when it is supplied to soil are the most important.

The author has intended the application of theories obtained by studies carried out in laboratories to practical manufacture of superphosphate and to its practical supply to the field. He has manufactured a non-retrograding superphosphate by addition of lyophilic amphoteric colloid substances to superphosphate, which did not retrograde to insoluble form by storage for a long time, retained its phosphoric acid water-soluble in soil and had a greater availability to plants. Thus more than 30 years have already elapsed since the author has engaged himself in these studies. One part of his studies designated as the Japanese Patent No. 71316 is now practically applied to the manufacture of non-

retrograding supesphosphate. It need not mention, therefore, that the present studies affect remarkable effects upon the agriculture and also upon the increased production of foodstuffs.

The author wishes to express his heartiest thanks to Prof. Emer. Dr. K. Miyake under whose valuable guidance and constant encouragement the present work has been completed. He is also very grateful to Prof. Emer. Dr. T. Tadokoro, Prof. Dr. Y. Nakamura and Prof. Dr. Y. Ishizuka for their kind advices and valuable suggestions throughout the present work.

Chapter 2.

The manufacture of non-retrograding superphosphate

"The non-retrograding superphosphates" which are named according to the Japanese Patent No. 71316 of the author, are obtained by good mixing of an ordinary superphosphate, made by the action of sulphuric acid on rock phosphate, and a proper quantity of a gelatine solution or by treatment with sulphuric acid of a mixture of rock phosphate and pupa refuse. They are, therefore, superphosphate affixing colloid substance or humin substance. To ascertain their non-retrograding property, the author has estimated the changes of amounts of their water-soluble phosphate during their storage and has obtained the following results.

§ 1. The effects of the addition of lyophilic amphoteric colloid substances upon the retrogradation of superphosphate during its storage.

I. The superphosphate.

The superphosphate was manufactured on November 16 1936. As the Florida rock phosphate, used as raw material, contained less than 3.0% of iron oxide and alumina, a powdered aluminium phosphate rock was added to increase the iron oxide and alumina content of the resulting superphosphate, namely to 100 parts rock phosphate were added 2.31 parts aluminium phosphate rock, The analytical results of raw material were shown in the following Table 1.

Table 1.
The composition of Florida rock
phosphate, aluminium phosphate rock
and mixed rock phosphate powder.

	Water	Total phosphoric acid	Total iron oxide and alumina
Florida rock phosphate	1.21%	31.11%	2.31%
Aluminium phosphate rock	9.66	35.33	32.03
Mixed rock phosphate powder	1.32	31.99	3.04

To 100 parts mixed rock phosphate powder were added 100 parts sulphuric acid (50° B), the materials were thoroughly mixed, accumulated in a reaction chamber. When the reaction was completed, the resulting mass was finely powdered. Its composition was analyzed as follows.

Table 2.
Composition of superphosphate.

	Water	Phosphoric acid			Total iron oxide and alumina
		Free	Total	Water-soluble	
Superphosphate	13.47%	5.93%	18.29%	16.13%	1.88%

A part of the superphosphate was stored in a glass-stoppered glass bottle; from time to time the quantities of its water-soluble and total phosphoric acid were estimated. The results were recalculated on the basis of a constant water content and tabulated in the following Table 3.

Table 3.
The changes of the composition of stored
superphosphate (Calculated on the basis of
a constant water content)

Date of estimation	Water	Phosphoric acid			Total iron oxide and alumina
		Free	Total	Water-soluble	
Nov. 11 1936	11.0	6.08	18.75	16.54	1.93
May 23 1937	11.0	5.46	18.43	16.21	1.85
June 26 1937	11.0	5.40	18.64	16.04	1.78
July 26 1937	11.0	5.39	18.91	16.20	1.88

August 14 1937	11.0	4.03	18.89	16.44	1.92
Sept. 8 1937	11.0	4.03	18.82	16.42	1.89
Oct. 22 1937	11.0	4.03	18.88	16.44	1.92
April 8 1938	11.0	4.03	18.76	16.32	1.92
May 10 1938	11.0	4.01	18.76	16.03	1.91
Jan. 27 1941	11.0	3.26	18.71	14.87	1.91
April 8 1941	11.0	3.22	18.47	14.80	1.91

It was seen from Table 3, that the superphosphate made from raw material containing about 3 % iron oxide and alumina did scarcely retrograde for 2 years long, an increase of water-soluble phosphoric acid was caused by an after-effect, However, thence a tendency of slight retrogradation was observed. When the superphosphate was stored for 4 years, its retrogradation appeared very distinctly.

When the non-retrograding property of a phosphate manure is to be discussed, it is advisable to use a superphosphate rich in iron oxide and alumina as starting material, so that a swift change of soluble phosphate to an insoluble form may be expected. In the practical manufacture, however, a raw material of such a high iron oxide and alumina content not being used, the author has performed his examinations within the highest limits practically allowed. Notwithstanding the comparatively small quantities of iron oxide and alumina, they were still sufficient to ascertain the tendencies of change of superphosphate occurred during the storage. Thus the above results indicated it clearly, that the author's considerations here mentioned were not at all erroneous.

II. The lyophilic amphoteric colloid substances added superphosphate.

The superphosphate manufactured according to the method of the author's Japanese Patent No. 71316 "the manufacture of the non-retrograding superphosphate" is called hereafter "the colloid substance added superphosphate". It was made by mixing the superphosphate shown in Table 2, i, e, its total phosphoric acid content 18.29 % and a gelatine of 14.21 % nitrogen content. According to Flieg (4) the best result was to be expected by mixing 1 part humate and 4 parts rock phosphate or 4 parts phosphoric acid. In the present investigation, gelatine was used and for the purpose of obtaining a 2.0 % nitrogen content product, 100

parts superphosphate and 16.6 parts gelatine, i. e. in the ratio of 1 gelatine to 6 superphosphate were taken. An aqueous solution of gelatine was mixed thoroughly to superphosphate, the mixture was dried, powdered and stored in a glass-stoppered glass bottle. The analysis and recalculation were carried out in the same way as stated in Article I. The following Table 4 shows the results obtained.

Table 4.

The changes of the composition of stored gelatine added superphosphate (Calculated on the basis of a constant water content, i. e. 5.0 %).

Date of estimation	Phosphoric acid			Total nitrogen	Total iron oxide and alumina
	Free	Total	Water-soluble		
Nov. 11 1936	5.33	16.77	14.12	2.05	1.61
May 23 1937	5.34	16.95	14.22	2.07	1.71
June 26 1937	5.35	17.01	14.09	2.01	1.67
July 26 1937	5.36	16.89	13.80	2.01	1.72
August 14 1937	5.36	16.82	14.16	2.01	1.72
Sept. 8 1937	5.38	16.59	13.97	2.21	1.72
Oct. 22 1937	5.36	16.88	13.91	2.01	1.72
April 8 1938	5.37	17.03	14.18	2.20	1.72
May 10 1938	5.37	17.01	14.21	2.21	1.72
Jan. 27 1941	5.32	17.48	14.14	2.10	1.71
April 8 1941	5.32	17.54	14.12	2.10	1.71

It was seen from Table 4, that the content of water-soluble phosphoric acid in gelatine added superphosphate was scarcely changed during the whole period of storage.

III. The humin substances added superphosphate.

This was also an example of "the colloid substance added superphosphate" manufactured according to the method of the author's same Patent. Above mentioned Florida rock phosphate and a pupa refuse of 10.15 % nitrogen content produced in the Province of Antung, Manchuria were selected as raw materials. One hundred parts of rock phosphate powder, 40 parts of the pupa refuse and 100 parts of sulphuric acid (50°

B). i. e. in a ratio of 1 pupa refuse to 2.5 rock phosphate were mixed well and stored in reaction chamber for a suitable time, during this time pupa refuse was changed to humin substances by the action of acid and heat of reaction. The resulting substance was rich in protein substances and decomposition products of protein substances. After the reaction time, the product was powdered and stored in a glass-stoppered glass bottle, analyzed and recalculated in the same way as stated in Article I. The following Table 5 shows the results obtained.

Table 5.

The changes of the composition of stored humin substances added superphosphate (Calculated on the basis of a constant water content, i.e. 10.0 %),

Date of estimation	Phosphoric acid			Total nitrogen	Total iron oxide and alumina
	Free	Total	Water-soluble		
Nov. 11 1936	7.00	15.26	12.48	1.42	1.30
May 23 1937	6.83	15.65	12.14	1.45	1.24
June 26 1937	6.87	15.36	12.55	1.47	1.35
August 14 1937	6.85	15.03	12.17	1.40	1.29
Sept. 8 1937	6.86	15.23	12.39	1.40	1.24
Oct. 22 1937	5.46	15.13	12.30	1.44	1.29
April 8 1938	5.45	15.45	12.46	1.46	1.34
May 10 1938	5.45	15.39	12.47	1.49	1.29
Jan. 27 1941	5.24	15.42	12.31	1.44	1.30
April 8 1941	5.18	15.55	12.38	1.44	1.30

It was seen from Table 5, that the retrogradation of humin substances added superphosphate was scarcely to be observed.

Examining the above mentioned results, it was possible to state as follows; namely when superphosphate manufactured by the ordinary method was stored for a long period, it retrograded gradually to an insoluble form, the quantities of water-soluble and free phosphoric acid were decreased gradually. Nevertheless, the non-retrograding superphosphate manufactured by the author's method showed almost no changes on quantities of water-soluble and free phosphoric acid, i. e. it did sca-

rcely retrograde to an insoluble form.

§ 2. Considerations.

When superphosphate is stored for a long period, it gives rise to a retrogradation phenomenon. The soluble calcium phosphate changes to insoluble iron phosphate and insoluble aluminium phosphate, especially to the former by this phenomenon. The chemical changes are said to proceed as the following equations indicate.

1. $\text{Ca H}_4 (\text{PO}_4)_2 \cdot \text{H}_2\text{O} + 5\text{H}_2\text{O} + \text{Fe} (\text{SO}_4)_3$
 $= 2 (\text{Fe PO}_4 \cdot 2\text{H}_2\text{O}) + 2\text{H}_2\text{SO}_4 + \text{Ca SO}_4 \cdot 2\text{H}_2\text{O}$
2. $\text{H}_2\text{SO}_4 + \text{Ca H}_4 (\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$
 $= \text{Ca SO}_4 \cdot 2\text{H}_2\text{O} + 2\text{H}_3\text{PO}_4$
3. $4\text{H}_3\text{PO}_4 + 2 (\text{Fe PO}_4 \cdot 2\text{H}_2\text{O}) = 2[\text{Fe H}_6 (\text{PO}_4)_3] + 4\text{H}_2\text{O}$
4. $2 [\text{Fe H}_6 (\text{PO}_4)_3] = 2 [\text{Fe H}_3 (\text{PO}_4)_2] + 2\text{H}_3\text{PO}_4$
5. $2 [\text{Fe H}_3 (\text{PO}_4)_2] = 2\text{Fe PO}_4 + 2\text{H}_3\text{PO}_4$

A superphosphate, which contains abundant quantities of iron oxide and alumina, gives rise not only to these unfavourable changes but an increase of its hygroscopicity. Accordingly, more moisture would be absorbed by the superphosphate. Thus the quality of superphosphate grows worse and worse.

As the author has stored his materials in glass-stoppered glass bottles sealed tightly, it was believed that no marked changes of water contents of the materials had occurred during the whole storage period. However, the comparatively better superphosphate with such a low iron oxide and alumina contents showed more or less retrogradation after its storage of 2 years, and marked retrogradation after 4 years. This indicated that the above mentioned reaction have been produced by the iron oxide and alumina of the material, and soluble phosphate was gradually changed to insoluble form. In case of a superphosphate of higher iron oxide and alumina content, these reactions should be intensified. When superphosphate was added to a base which contained abundant quantities of iron oxide and alumina, for example to a soil, it was not hard to suppose that these reactions should occur very rapidly to a considerable extent.

On the contrary, non-retrograding superphosphate of the author did scarcely retrograde even if it was stored for 4 years. This was an important influence of added gelatine or decomposition products of pupa

refuse and made an important account of the author's patent. Gelatine and decomposition products of pupa refuse here added belong to protein and are to be regarded as typical lyophilic amphoteric colloid substances. When they were mixed with superphosphate, there occurred many colloid chemical reactions between them, such as mutual adsorption, and also many stoichiometrical reactions between them. Accordingly, many complex adsorption compounds would be formed, which retarded markedly the above mentioned reactions between superphosphate and iron oxide and alumina. It could be also rationally deduced, that these lyophilic amphoteric colloid substances combined not only with phosphoric acid but with iron oxide or alumina, that the quantities of iron oxide and alumina which would react with superphosphate decreased markedly, and that the retrogradation reactions between superphosphate and iron oxide or alumina were greatly inhibited.

It will be then very natural to question "what is the protective action of these lyophilic amphoteric colloid substances against the retrogradation of superphosphate?". One of many reasons of the present investigation is to solve this question.

Concerning this problem, not many investigations have been reported. Especially there was none that agreed with the author's investigation object. However, the following ones may be mentioned.

Van Bemmelen (1) stated that when humin substances, proteins, glycerine, sugars, bases and salts were added to soils, they dissolved out silicic acid, iron oxide, alumina and alkali earths and at the same time phosphoric acid of soils, that therefore a great many quantities of phosphoric acid could be found in soil solution. He also stated that the reason of this solubility was due to formation of a soluble colloidal molecular complex between the added substances and phosphate ion.

According to Brintzinger and Beier (7), the solvent power of humin substance upon phosphoric acid was one general effect of hydrophilic colloids, which was caused by their capillary activity.

Demalon and Bastisse (8) stated that the increase of solubility of phosphoric acid by the addition of organic bases was caused by their anion effects, that all sorts of anions had not the same effects, so that they could be divided into active anions and inactive anions, and that the humic acid anion belonged to the active group.

Scheffer and Hausman (9) concluded that humic substances, soil

humus and stable manure increased the solubility of phosphates of all kinds in soil.

As has been already stated in Chapter 1, Mack, Spencer and Stewart, Flieg, Scharrer and Keller, Rautenberg sustained that the solubility of phosphate in soil received a favorable effect from humic substances and stable manure.

Putting these things together, the author comes to the following conclusion. When phosphoric acid is supplied to soil in the form of soluble phosphate fertilizer, its chemical availability is marked in consequence of its water-solubility. As it dissolves in soil solution and distributes sufficiently throughout the soil, it results that its movability and its positional availability are very marked. However, in consequence of its marked water-solubility, it combines with iron oxide, lime and alumina of soil, turns to an insoluble form and decreases extremely its chemical and positional availabilities.

If a stable manure, humic substances or generally a lyophilic colloid are added to soil or if phosphoric acid is added to soil in a form which does not produce free phosphoric acid ion, namely in a form of organic phosphoric acid compounds, the movability of phosphoric acid is held for a long period, chemical and positional availabilities are markedly increased.

Chapter 3.

The theoretical basis of the manufacture of non-retrograding superphosphate.

It was clearly indicated from the experimental results of Chapter 1 that, according to the procedure of the author's Patent, non-retrograding superphosphate which did not retrograde to insoluble form by a long time-storage could be manufactured. When proteins or humin substances derived from protein were added to superphosphate in a ratio of 6:1 or when they are added to rock phosphate in a ratio of 2.5:1 at the manufacture of superphosphate, the non-retrograding property of the manufactured goods were markedly increased. It should be an important theoretical basis of the manufacture of non-retrograding superphosphate to know why such lyophilic amphoteric colloid substances as proteins or their derivatives show this favourable characteristic. When this question is answered and the non-retrograding property is theoretically

explained, practical techniques of its manufacture can be expected to be surely established. Therefore, the studies concerning the theoretical explanation of non-retrograding property are important factors for the establishment of practical technique. The author has examined the effects of lyophilic amphoteric colloid substances upon water-soluble phosphoric acid ion for the purpose of confirming the basis of the present investigations. This is the reason of undertaking this Chapter and it may be superfluous to point to the importance of the examinations performed in it.

§ 1. The effects of lyophilic amphoteric colloid substances upon electrical conductivity of superphosphate solution.

The electrical conductivities of salt solutions are important measures which indicate the quantities of ions existing in them. When other substances, especially lyophilic amphoteric colloid substances, are added to solutions, the salts in them react with the added substances, the dissociations of salts are increased or decreased, and consequently the quantities of ions in the solutions are changed. One observes, therefore, the changes of their electrical conductivity. The author has performed the following examinations using superphosphate to know the effects here mentioned. The analytical results of superphosphate are shown in Table 6.

Table 6.
The composition of superphosphate.

Phosphoric acid		Water-soluble				
Water-soluble	Free	CaO	H ₂ SO ₄	FeO ₃	Al ₂ O ₃	MgO
19.93	3.54	12.95	11.24	0.38	0.44	0.75

The electrical conductivities of superphosphate solutions of different concentrations were measured at 17°C. The figures of Tabel 7 were the mean values of three determinations.

Table 7.
The conductivities of superphosphate
solutions of different concentrations.
(Mho)

Concentration (%)	1	2	3	4	5
Conductivity	4.8. 10^{-3}	7.95	10.94	13.25	15.51
Concentration	6	7	8	9	10
Conductivity	17.85	19.88	22.03	23.76	25.38

According to this Table, it was seen that the electrical conductivities increased with the increase of the concentrations of superphosphate. The relation between electrical conductivities and concentrations was almost linear, as generally accepted by those of many electrolytes. Therefore, it could be deduced that the dissociation of superphosphate decreases when its concentration increases.

To determine the electrical conductivities of superphosphate solution by addition of lyophilic amphotetic colloid substances, the author has used peptone, gelatine and gum acacia as lyophilic amphoteric colloid substances to be added, examined as described below.

Reagents.

1. 2 % superphosphate solution.
2. 1 % peptone solution (dissolved Witte peptone in water).
3. 1 % gelatine solution (dissolved pure gelatine White Bear brand for photographic plates, made in Germany, in water).
4. 2 % gum acacia solution (dissolved gum acacia Merck in water).

I The case of peptone.

In four 100 cc. measuring flasks 1) 50 cc. superphosphate solution were taken, made up to 100 cc. with water, used as standard, 2) 50 cc. superphosphate solution and 10 cc. peptone solution were taken, made up to 100 cc. with water, 3) 50 cc. superphosphate solution and 30 cc. peptone solution were taken, made up to 100 cc. with water, 4) 50 cc. superphosphate solution and 50 cc. peptone solution were taken. They were shaken well, stood over night at 10–12°C. In four parchment paper dialysers of Central Scientific Co. U. S. A. were taken 20 cc. of each solution prepared as mentioned above, the dialysers were kept in four beakers of same size which contained 70 cc. water, the whole was

let stand at 10°C. for 1 hour. After this time fresh beakers were given to each dialyser. The electrical conductivity of each beaker content, i.e. the electrical conductivities of the outer solutions of dialysis were determined at 17°C. The following results were the mean values of the three determinations.

Table 8.

The electrical conductivities of the outer solutions of dialysis of superphosphate solutions added with peptone (Mho, 17°C.)

Number of times of exchange of beakers	Standard	Peptone solution added		
		10 cc.	30 cc.	50 cc.
1st	43.63. 10 ⁻⁵	36.23	26.14	23.26
2nd	31.37	27.03	21.51	18.50
3rd	25.82	22.27	18.25	15.77

II The case of gelatine.

The same experiments as in the case of peptone were carried out with use of gelatine instead of peptone, with the following results.

Table 9.

The electrical conductivities of the outer solutions of dialysis of superphosphate solutions added with gelatine (Mho, 17°C.)

Number of times of exchange of beakers	Standard	Gelatine solution added		
		10 cc.	30 cc.	50 cc.
1st	43.63. 10 ⁻⁵	39.76	32.42	26.96
2nd	31.37	29.07	27.82	23.67
3rd	25.82	23.64	20.75	18.73

III The case of gum acacia

With the use of gum acacia instead of peptone or gelatine, the same experiments were carried out with the following results.

Table 10.

The electrical conductivities of the outer solutions of dialysis of superphosphate solutions added with gum acacia (Mho, 17°C.)

Number of times of exchange of beakers	Standard	Gum acacia solution added		
		10 cc.	30 cc.	50 cc.
1st	43.63. 10 ⁻⁵	38.31	33.67	30.63
2nd	31.37	28.17	27.06	25.58
3rd	25.82	25.03	23.96	22.86

According to the Tables 8, 9, 10, it was seen that the electrical conductivities of the outer solution decreased by the increase of time of dialysis both in the case of superphosphate and in the case of addition of lyophilic amphoteric colloid substances, it was, therefore, known that the quantities of the dialysable dissociated parts of superphosphate decreased by dialysis. By addition of lyophilic amphoteric colloid substances to superphosphate solution, the quantities of the dialysable dissociated part of the latter decreased. The decreases of the quantities of the dialysable dissociated parts were the more sufficient, when more quantities of lyophilic amphoteric colloid substances were added, as was seen from the fact that the electrical conductivities decreased gradually as additional quantities of lyophilic amphoteric colloid substances increased. Among the effects of additional lyophilic amphoteric colloid substances, the greatest effect was observed by peptone, followed by gelatine, the effect of gum acacia was the smallest.

It was, therefore, deduced, that when lyophilic amphoteric colloid substances were added to superphosphate solution, the dissociation of superphosphate was inhibited, the quantity of ions which diffused into outer solution by dialysis was decreased, the electrical conductivity of the outer solution sank, and the effect was the greatest by peptone, followed by gelatine, the smallest by gum acacia.

§ 2. The effects of lyophilic amphoteric colloid substances upon the dialysis of phosphate ion of superphosphate solutions.

It was observed by the former experiments, that the quantity of ions which diffused into outer solution by dialysis was decreased when lyophilic amphoteric colloid substances were added to superphosphate solutions. For the purpose of learning the behavior of phosphate ion by the same treatment, the author has carried out the following experiments.

As the working, solutions 5 % superphosphate solution (0.9965 g P_2O_5 in 100 cc. solution), 1 % Witte peptone solution and 1 % gelatine (White Bear brand, made in Germany) were chosen. In four 100 cc. measuring flasks 1) 50 cc. superphosphate solution were taken, made up to 100 cc. with water, used as the standard, 2) 50 cc. superphosphate solution and 10 cc. gelatine solution were taken, made up to 100 cc. with water, 3) 50 cc. superphosphate solution and 30 cc. gelatine solution were taken, made up to 100 cc. with water, 4) 50 cc. superphosphate solution and 50 cc. gelatine solution were taken. The same procedures were also conducted using peptone instead of gelatine.

The mixtures were shaken well, stood over night. In four parchment paper dialysers of Central Scientific Co. U.S.A. were taken 20 cc. of each solution, the dialysers were kept in four beakers which contained 50 cc. water. After 1 hour, the outer solution was exchanged with 50 cc. water, then after 2 hours and after still 3 hours the outer solution was exchanged in the same way. The quantities of phosphoric acid diffused into the outer solutions were estimated according to molybdc method. The following Table II indicated the mean values of 3 determinations. The room temperature during these experiments was 10–13°C.

Table II.

The quantities of dialyzed phosphoric acid by addition of gelatine or peptone to superphosphate solution. (P_2O_5 , mg)

Duration of dialysis	Standard	Gelatine solution added			Peptone solution added		
		10 cc.	30 cc.	50 cc.	10 cc.	30 cc.	50 cc.
1 hour	10.65	9.76	8.55	6.12	10.18	9.05	6.75
2 hours	13.15	12.82	11.48	7.02	12.88	12.67	8.77
3 hours	10.84	10.55	10.03	6.63	10.56	10.51	10.46

It was seen from this table, that the quantities of dialysable

phosphate ion were decreased by addition of lyophilic amphoteric colloid substances, that the more lyophilic amphoteric colloid substances were added, the greater was the depression. If the effects of gelatine and peptone were compared, it was evident that the effect was greater by gelatine than by peptone.

§ 3. The effects of lyophilic amphoteric colloid substances upon the inversion of sucrose caused by hydrogen ion of superphosphate solution.

To make clear the effects of lyophilic amphoteric colloid substances upon the hydrogen ion concentration of superphosphate solution and also to determine the hydrogen ion concentration of superphosphate solution, the author has carried out the inversion of sucrose as follows.

As the working solutions, 5 % superphosphate solution, 1 % Witte peptone solution, 1 % gelatine solution (White Bear brand, made in Germany) and 1 % saccharose Merck solution were chosen. Superphosphate solution and lyophilic amphoteric colloid substance solution were mixed in the same way as described in § 2. In four 100 cc. measuring flasks 1) 20 cc. superphosphate and 80 cc. saccharose solution were taken, used as the standard, 2) 20 cc. superphosphate to which 10 cc. gelatine solution were added and 80 cc. saccharose solution were taken, 3) 20 cc. superphosphate solution to which 30 cc. gelatine solution had been added and 80 cc. saccharose solution were taken, 4) 20 cc. superphosphate solution to which 50 cc. gelatine solution had been added and 80 cc. saccharose solution were taken. The four flasks were immersed in boiling water bath simultaneously for 30 minutes to obtain the inversion of saccharose. After that the solution was cooled, and with 20 cc. solution (which contained 160 mg saccharose, equivalent to 169.41 mg invert sugar) the quantities of invert sugar were determined by the Bertrand's method. The following are the mean values of 2 determinations.

Using peptone solution instead of gelatine solution, the same procedures were carried out.

Table 12.

The inversion of saccharose by superphosphate solution and by lyophilic colloid substances added superphosphate solutions.

		Invert sugar (mg)	% of invert sugar to original solution
Original solution		168.41	100.00
Standard		33.41	19.84
Gelatine solution added	10 cc.	28.05	16.66
	30 cc.	24.95	14.82
	50 cc.	22.26	13.22
Peptone solution added	10 cc.	27.53	16.35
	30 cc.	24.19	14.36
	50 cc.	16.56	9.83

It was seen from this Table, that the superphosphate solution decreased its saccharose inverting power by addition of lyophilic amphoteric colloid substances. As the power was said to be in proportional relation with the free hydrogen ion concentration of the solution, it could be deduced that the hydrogen ion concentrations of superphosphate solutions were decreased by addition of lyophilic amphoteric colloid substances and that the diminution was greater, the greater the quantities of added substances. The degree of diminution was greater by addition of peptone than by that of gelatine. Thus it was known that lyophilic amphoteric colloid substances decreased the hydrogen ion concentrations of superphosphate solution, and that the effect was greater by peptone than by gelatine.

§ 4. The effects of lyophilic amphoteric colloid substances upon the reactions between phosphate ion of superphosphate and bases or soils.

The reactions between phosphate ion and bases or soils are influenced greatly by the pH value of the reaction medium. However, the present investigations were intended not to know the effects of bases or soils upon phosphate ion, but to know the colloid chemical effects

of lyophilic amphoteric colloid substances when they were added to the mixture of bases or soils and phosphate ion. The present investigations were no examinations concerning the solubilities of phosphate ion in the strict sense of the word. It was, therefore, believed that even though the influences of pH values of reaction medium were so enormous, there was no objection to the present investigation when they were left out of consideration.

I. The preparation of materials and reagents.

A. 2 % superphosphate solution. The compositions of 2 % superphosphate solution were as follows.

Table 13.

The compositions of 2 % superphosphate solution. (mg in 100 cc.)

Phosphoric acid (P_2O_5)		Water-soluble			
Water-soluble	Free	Fe_2O_3	Al_2O_3	CaO	SO_3
325.8	69.4	1.8	1.1	174.6	116.6

B. CaO solution. CaO (Takeda) was dissolved in water, the solution was filtered and stored in a dark cool place.

C. MgO (Takeda)

D. $Fe(OH)_3$. From $FeCl_3$ solution, it was precipitated by addition of ammonia, the precipitate was washed until no chlorine was observed. It was used in wet state.

E. $Al(OH)_3$. From $AlCl_3 \cdot H_2O$ solution, it was obtained and used in the same way as in the case of $Fe(OH)_3$ described in D.

F. Soils. 1) The soil collected from the forest of Shin-nobe, Befu Machi, Hyogo Prefecture. 2) The soil collected from the neighborhood of Itami Station, Itami Shi, Hyogo Prefecture. 3) A special soil collected from Isurugi-Mura, Nishitonamigun Toyama Prefecture.

Table 14.

The chemical compositions of soils.

	Befu-Soil	Itami-Soil	Toyama-Soil
Water	1.01	1.14	5.79
Loss on ignition	2.97	4.33	2.41
Humine substances	1.59	1.51	0.75

Total nitrogen	0.10	0.12	0.04
Hot HCl insoluble	92.40	87.53	75.82
Hot HCl soluble			
Iron oxide	0.93	2.55	10.46
Alumina	0.87	2.53	3.32
Phosphoric acid P ₂ O ₅	0.14	0.24	0.23
Manganese oxide	0.12	0.32	0.34
Calcium oxide	0.22	0.27	0.64
Magnesia	0.03	0.60	0.83
Sulphuric acid SO ₃	0.07	0.04	0.02
Kali	0.09	0.19	0.20
Soda	0.11	0.34	0.59
Silicic acid	0.76	0.55	0.31
Exchange acidity (KCl method)	6.30	3.87	3.81

G. Gelatine. Kokko brand, made by Nitta Leather Manufacturing Co. Its nitrogen content being 14.71 %, was used as 1 % solution.

H. Peptone. Made by Witte Co. Its nitrogen content being 14.4 %, was used as 1 % solution.

II. Experiments.

A. CaO.

In four 100 cc. measuring flasks 1) 20 cc. superphosphate solution were taken, added 10 cc. CaO solution, made up to 100 cc. with water, used as a standard, 2) 20 cc. superphosphate solution and 10 cc. gelatine solution were taken, the mixture was shaken occasionally, stood over night, then added 10 cc. CaO solution, and made up to 100 cc. with water, 3) 20 cc. superphosphate solution and 30 cc. gelatine solution were taken, the mixture was shaken occasionally, stood over night, then added 10 cc. CaO solution, and made up to 100 cc. with water, 4) 20 cc. superphosphate solution and 50 cc. gelatine solution were taken, the mixture was shaken occasionally, stood over night, then added 10 cc. CaO solution, and made up to 100 cc. with water.

They were let stand over night and filtered. The quantities of phosphoric acid were determined according to the molybdc method

with 20 cc. filtrate. In the original 20 cc. superphosphate solution had to be contained 14.11 mg P_2O_5 .

Using peptone instead of gelatine, the same procedures were carried out. The following are the mean values of 2 determinations.

Table 15.

The effects of CaO upon water-soluble phosphoric acid of superphosphate solution, added with and without gelatine or peptone.

	Phosphoric acid (mg)		Proportion to original solution
Original solution		14.11	100.00
Standard		13.91	92.00
Gelatine solution added	10 cc.	13.52	98.52
	30 cc.	13.91	98.58
	50 cc.	14.10	99.93
Peptone solution added	10 cc.	13.20	93.55
	30 cc.	13.33	94.47
	50 cc.	13.59	96.31

B. MgO.

The same procedures were carried out as in the case of CaO solution using 0.05 g MgO, instead of 10 cc. CaO solution, with the following results.

Table 16.

The effect of MgO upon water-soluble phosphoric acid of superphosphate solution, added with and without gelatine or peptone.

	Phosphoric acid (mg)		Proportion to original solution
Original solution		14.11	100.00
Standard		6.83	48.41
Gelatine solution added	10 cc.	7.59	53.79
	30 cc.	8.68	61.52
	50 cc.	9.63	68.25
	10 cc.	7.38	52.30

Peptone solution added	30 cc.	8.17	57.90
	50 cc.	9.05	64.14

C. $\text{Fe}(\text{OH})_3$.

To a solution which contained 0.05 g FeCl_3 was added ammonia, the precipitated $\text{Fe}(\text{OH})_3$ was boiled, filtered, and washed well with water until no Cl^- was observed. The same procedures were carried out as in the cases A and B, using the obtained $\text{Fe}(\text{OH})_3$ instead of CaO or MgO with the following results.

Table 17.

The effects of $\text{Fe}(\text{OH})_3$ upon water-soluble phosphoric acid of superphosphate solution, added with and without gelatine or peptone.

	Phosphoric acid (mg)		Proportion to original solution
Original solution		14.11	100.00
Standard		12.63	89.51
Gelatine solution added	10 cc.	13.14	93.13
	30 cc.	13.26	93.98
	50 cc.	13.40	94.97
Peptone solution added	10 cc.	12.95	91.78
	30 cc.	13.03	92.35
	50 cc.	13.27	94.05

D $\text{Al}(\text{OH})_3$.

The same procedures were carried out as in the case of $\text{Fe}(\text{OH})_3$ using 0.05 g $\text{AlCl}_3 \cdot \text{H}_2\text{O}$ instead of FeCl_3 with the following results.

Table 18.

The effects of $\text{Al}(\text{OH})_3$ upon water-soluble phosphoric acid of superphosphate solution, added with and without gelatine or peptone.

	Phosphoric acid (mg)		Proportion to original solution
Original solution		14.11	100.00
Standard		13.33	94.47

Gelatine solution added	10 cc.	13.65	96.74
	30 cc.	13.97	99.01
	50 cc.	14.10	99.93
Peptone solution added	10 cc.	13.45	95.32
	30 cc.	13.72	97.24
	50 cc.	13.95	98.87

E. Soils.

I. Befu-Soil.

To superphosphate solution treated with gelatine or peptone in the same way as described above were added 10 g soil. The other procedures were not changed from those of the above mentioned, A, B, C and D.

Table 19.

The effects of Befu-Soil upon water-soluble phosphoric acid of superphosphate solution, added with and without gelatine or peptone.

		Phosphoric acid (mg)	Proportion to original sol- ution
Original solution		14.11	100.00
Standard		12.89	91.35
Gelatine solution added	10 cc.	13.14	93.13
	30 cc.	13.46	95.39
	50 cc.	13.83	98.02
Peptone solution added	10 cc.	13.05	92.49
	30 cc.	13.38	94.83
	50 cc.	13.59	96.31

2. Itami-Soil.

The same procedures were carried out using Itami-Soil.

Table 20.

The effects of Itami-Soil upon water-soluble phosphoric acid of superphosphate solution, added with and without gelatine or peptone.

	Phosphoric acid (mg)		Proportion to original solution
Original solution		14.11	100.00
Standard		12.44	88.16
Gelatine solution added	10 cc.	12.76	90.43
	30 cc.	13.01	92.20
	50 cc.	13.20	93.55
Peptone solution added	10 cc.	12.54	88.87
	30 cc.	12.80	90.72
	50 cc.	13.05	92.49

3. Toyama-Soil.

The same procedures were carried out using Toyama-Soil.

Table 21.

The effects of Toyama-Soil upon water-soluble phosphoric acid of superphosphate solution, added with and without gelatine or peptone.

	Phosphoric acid (mg)		Proportion to original solution
Original solution		14.11	100.00
Standard		8.23	58.33
Gelatine solution added	10 cc.	8.42	59.67
	30 cc.	8.87	62.86
	50 cc.	9.44	66.90
Peptone solution added	10 cc.	8.36	59.25
	30 cc.	8.80	62.37
	50 cc.	9.18	65.06

The influence of pH values of the reaction medium were left out of consideration on the basis of reasons stated in the beginning of this paragraph, 92.20 % of water-soluble phosphoric acid were still in soluble form, and the 7.80 % were changed to insoluble form when CaO solution was added to the superphosphate solution. When gelatine or peptone was added to it, the formation of insoluble phosphate caused by the addition of CaO was inhibited and the greater the quantities of

added substances, the greater was inhibition. When gelatine and peptone were compared, the effect of the former was greater than that of the latter. The greater quantities of soluble phosphoric acid were observed by gelatine than by peptone if the same quantities of them were added.

Concerning the effects of MgO upon superphosphate solution, 0.05 g MgO was added. As 0.0079 g MgO is equivalent to 0.011 g CaO, it became evident that $0.03/0.0079=6.33$ fold quantities of MgO were added compared to addition of CaO. As 0.011 g CaO had changed 7.80 % phosphoric acid to an insoluble form and if it would be assumed that MgO and CaO had the same influences, $7.8 \times 6.33=49.37$ % phosphoric acid should be changed to insoluble form. Therefore, $14.11 (100-49.37) = 7.15$ mg phosphoric acid should be kept in solution as a soluble form. However, the result of the investigation showed that only 6.38 mg phosphoric acid was soluble, the difference of both figures, i.e. $7.15-6.38=0.77$ mg phosphoric acid was superfluously changed to an insoluble form. So it was known that the effect of MgO was superior to that of CaO and that by addition of MgO greater quantities of phosphoric acid were changed into insoluble form than by CaO. When gelatine or peptone was added to it, the effect of MgO was decreased and the greater the quantities of added substances, the greater was the diminution of the effect. The favourable effect of gelatine was greater than that of peptone.

In the case of $\text{Fe}(\text{OH})_3$, it was calculated in the same way as the effect of MgO, as follows. As 0.025 g FeCl_3 is equivalent to 0.011 g CaO, it became necessary that the 2 fold of $\text{Fe}(\text{OH})_3$ was added. Accordingly, the values of comparison should be $14.11 (100-7.8 \times 2) = 11.91$ mg. However, the experimental result was 12.63 mg, $12.63-11.91=0.72$ mg phosphoric acid was superfluously in soluble form. It was known that the effect of $\text{Fe}(\text{OH})_3$ was inferior to that of CaO. When gelatine or peptone was added to it, the diminution of quantities of water soluble phosphoric acid was decreased as in the former cases, the favourable effect was greater by gelatine than by peptone.

In the case of $\text{Al}(\text{OH})_3$, similar calculations as those of MgO and $\text{Fe}(\text{OH})_3$ were carried out. As 0.02 g $\text{AlCl}_3 \cdot \text{H}_2\text{O}$ is equivalent to 0.011 g CaO, it became necessary that the 2.5 fold of $\text{Al}(\text{OH})_3$ was added. Accordingly, values of comparison should be $14.11 (100-7.8 \times 2.5) = 11.36$ mg. However, the experimental result was 13.33 mg, $13.33-11.36=1.97$ mg

phosphoric acid was superfluously in the soluble form. It was known that the effect of $\text{Al}(\text{OH})_3$ was inferior to that of CaO and $\text{Fe}(\text{OH})_3$. The effects of gelatine or peptone were analogous to those of the other cases.

Considering the above calculations, it could be deduced that the power of MgO , CaO , $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ to change the soluble phosphoric acid into insoluble form was the greatest by MgO , followed by CaO and $\text{Fe}(\text{OH})_3$, the smallest by $\text{Al}(\text{OH})_3$. However, in the present investigation no attention had been paid to the pH values of the reaction medium according to the reasons stated already. The greatest efficiency was found in MgO , but it could be supposed as one of the reasons, that the reaction of medium would be inclined to more basic, when MgO was added than when CaO , $\text{Fe}(\text{OH})_3$ or $\text{Al}(\text{OH})_3$ was added; thus according to the strong basisty of the medium, the formation of insoluble Mg-phosphate was greater than in the other cases. Gelatine and peptone acted to inhibit the formation of insoluble salts. The effect of gelatine was always greater than that of peptone. It was verified that the inhibiting effects of lyophilic amphoteric colloid substances such as gelatine and peptone upon the formation of insoluble salts were observed notwithstanding the pH value of the reaction medium.

When soils were added to supephosphate solution, the quantities of soluble phosphoric acid were decreased. Among the effects of Befu-Soil, Itami-Soil and Toyama-Soil, the greatest one was observed in Toyama-Soil, namely 58.33 % were kept soluble and 41.67 % were changed to insoluble, following Itami-Soil with 88.16 % soluble and 11.84 % insoluble, and Befu-Soil with 91.35 % soluble and 8.65 % insoluble.

The effects of addition of gelatine or peptone were the same as those of the former experiments, thus the formation of insoluble phosphoric acid was inhibited and greater quantities were kept soluble. The favourable effects of gelatine were greater than those of peptone, this was quite similar as the former experiment.

Among the compositions of these soils, the contents of hot HCl soluble iron oxide, alumina, lime and magnesia were the greatest by Toyama-Soil, followed Itami-Soil, the smallest by Befu-Soil, but the content of humine substances was, on the contrary, the greatest in Befu-Soil, the smallest in Toyama-Soil. As was seen from the former experiments, these soluble bases decreased the quantities of soluble

phosphoric acid of superphosphate solution and at the same time the free humic acid made phosphoric acid soluble. Therefore, it could be accepted naturally that the formation of insoluble phosphoric acid was the greatest by Toyama-Soil, followed by Itami-Soil and Befu-Soil.

§ 5. The effects of lyophilic amphoteric colloid substances upon the reactions between phosphoric acid of superphosphate and soils when the reaction times or the quantities of soils were varied.

Accordingly to the experiments of the former paragraph, the effects of varied quantities of soil to be added and of varied lengths of reaction time were studied as stated in this paragraph.

The same soils as in the former paragraph were used, In nine 100 cc. measuring flasks, 20 cc. superphosphate solution were taken, to three of them were added 50 cc. gelatine solution, to three of them were added 50 cc. peptone solution, all were shaken well, stood over night, then 30 g soil were added, and made up to 100 cc. with water. After 24, 72 and 120 hours, the quantities of water-soluble phosphoric acid were determined with the results as shown in Table 22. The figures are the mean values of 2 determinations.

The same procedures were also carried out using 50 g. soil.

Table 22.

The effects of gelatine and peptone upon the soluble phosphoric acid of superphosphate, when soils were added in different quantities or the lengths of reaction time were varied.

1. Befu-Soil

Time (hours)		30 g soil Addition of			50 g soil Addition of		
		None	Gelatine	Peptone	None	Gelatine	Peptone
24	Phosphate (mg)	11.67	12.44	12.12	10.44	11.73	11.67
	Percentage	82.67	88.16	85.90	73.99	83.13	82.72
72	Phosphate (mg)	11.35	12.32	11.80	9.89	10.78	10.59
	Percentage	80.44	87.24	83.63	70.09	76.40	75.05

120	Phosphate (mg)	11.23	11.74	11.48	9.12	10.14	9.95
	Percentage	79.59	83.20	81.29	64.64	71.86	70.52

2. Itami-Soil

24	Phosphate (mg)	10.97	12.96	11.93	9.70	10.95	10.65
	Percentage	77.75	91.85	84.55	68.75	77.60	75.48
72	Phosphate (mg)	10.14	10.91	10.53	8.61	9.06	8.80
	Percentage	71.86	77.32	74.63	61.02	64.21	62.37
120	Phosphate (mg)	9.88	10.78	10.27	8.17	8.80	8.68
	Percentage	70.02	76.40	72.79	57.90	62.37	60.95

3. Toyama-Soil

24	Phosphate (mg)	2.36	4.08	3.38	0.89	1.59	1.40
	Percentage	16.73	28.92	23.95	6.31	11.27	9.92
72	Phosphate (mg)	2.04	2.68	2.42	0.38	1.02	0.89
	Percentage	14.46	18.99	17.15	2.69	7.23	6.31
120	Phosphate (mg)	0.56	2.23	1.66	0.19	0.89	0.64
	Percentage	3.97	15.80	11.76	1.35	6.31	4.54

By addition of soil to superphosphate solution, the decrease of quantities of soluble phosphoric acid was enlarged according as greater quantities of soils were added. It is generally accepted that the fixing action of phosphoric acid by addition of soils is completed within 24 hours. By the present investigation the decrease of quantity of soluble phosphoric acid was nearly completed within 24 hours in the cases of Befu-Soil and Itami-Soil, therefore, there were no marked enlargements of depression of soluble phosphoric acid by the contacts of 72 and 120 hours. The results coincided well with the generally accepted fact mentioned above. However, in the case of Toyama-Soil, the depression continued until the contact of 120 hours. It could be said that the fixing action of Toyama-Soil proceeded very slowly, and that Toyama-Soil proved to be a special soil. The effect of soils and that of addition of gelatine or peptone were entirely the same as those of the former experiments, the greatest by Toyama-Soil, followed by Itami-Soil and Befu-Soil, and the favourable effect of gelatine was greater than that

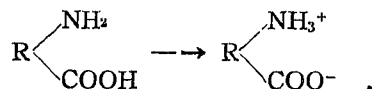
of peptone.

§ 6. Discussion.

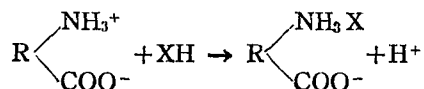
It was seen from the results of determination of the electrical conductivity, that superphosphate dissociated as a general electrolyte and that the conductivity increased with linear relations to its concentrations. When gelatine, peptone or gum acacia which belong to lyophilic amphoteric colloid substances was added to superphosphate solution, the ions formed by the dissociation of superphosphate decreased their diffusibility by dialysis. It could be said externally that the dissociation of superphosphate was depressed by the added lyophilic amphoteric colloid substances, and that the degree of depression was greater, the more of them were added. How could this external depression of dissociation occur? The added protein substances such as gelatine and peptone, and the added polysaccharide such as gum acacia belong to the so-called high molecular compounds. These high molecular compounds are generally substances of greater surface activity and they have a strong power to adsorb other substances and at the same time to be adsorbed by other substances.

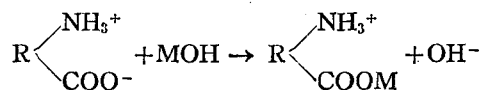
When such a substance with strong adsorption ability was added to a superphosphate solution, it was naturally to be presumed that the adsorption between the added substances and all sorts of ions of solution would occur. The ions were adsorbed by added lyophilic amphoteric colloid substances, therefore, when the mixture was dialysed, the quantities of ions which diffused out into the outer solution and the electrical conductivity of the outer solution decreased. Thus the external depression of dissociation of superphosphate was increased.

The lyophilic amphoteric colloid substances such as gelatine and peptone in solution dissociated and formed a zwitter ion as the following equation indicates



This zwitter ion reacts with other cations and anions of solution, and forms many sorts of salts as shown in the following equations.





Accordingly, when a protein substances such as gelatine or peptone was added to superphosphate solution, it reduced not only the quantities of free ions by adsorption, but it also decreased them by formation of salts with phosphate ion or other anions or cations. It was deduced that the external depression of dissociation of superphosphate by addition of gelatine or peptone was also effected according to formation of salts mentioned above. The formation of zwitter ion of gum acacia was very feeble, it was deduced that the depression happened mainly by adsorption and that the salt formation was not significant. It was observed that the effect of peptone was superior to that of gelatine. The reason of this difference may be that the decomposition was more or less advanced in the case of peptone than of gelatine, therefore, the former had more free amino groups and free carboxyl groups in its molecule than the latter, the formation of salts, according to the above equations, was greater by the peptone than by gelatine.

The quantities of phosphoric acid found in the outer solution of dialysis were decreased by addition of gelatine or peptone, the depression was greater the greater quantities of them were added, the effects of gelatine was superior to that of peptone, the dialyzed quantities of phosphoric acid were smaller by gelatine than by peptone. This was due to the decrease of free phosphoric acid according to adsorption by gelatine or by peptone and at the same time according to combination with gelatine or with peptone. The greater effect of gelatine made it clear that the adsorption and combination between phosphoric acid and gelatine were superior to those of peptone.

The hydrogen ion concentration of superphosphate solution decreased by the addition of gelatine or peptone. The effect was greater by peptone than by gelatine in contrast to phosphoric acid.

It was generally deduced that protein substances such as gelatine and peptone adsorbed and combined all sorts of ions in superphosphate solution, thus decreasing the quantities of free ions, and the effect of peptone was superior to that of gelatine. The action of gelatine upon phosphoric acid or generally upon anions was superior to that of peptone and that of peptone upon hydrogen ion or generally upon cations was

superior to that of gelatine. These were due to the differences of physical adsorbing power and of chemical combining power of both proteins and they are said to be the characteristics of both proteins.

When a base such as CaO, MgO, Fe(OH)₃ or Al(OH)₃ was added to superphosphate solution, its phosphoric acid reacted with the added bases, the quantities of free phosphoric acid were decreased, and hence the quantities of phosphoric acid determined by the molybdc method were decreased. The bases combined with phosphoric acid, and produced insoluble phosphates. When soils were added, the same results were observed. Among the three soils, the greatest effect was observed with Toyama-Soil, followed by Itami-Soil, the smallest with Befu-Soil. The contents of hot HCl soluble bases such as iron oxide, alumina, calcium oxide and magnesia were the greatest in Toyama-Soil, followed by Itami-Soil, the smallest in Befu-Soil. But the contents of humine substances were in reverse order. As has already been stated by the former experiment, such bases reacted with phosphoric acid and changed it into insoluble form, and as acid humine substances made it soluble on the contrary, the conclusion was evidently that the formation of insoluble phosphoric acid was the greatest in Toyama-Soil, followed by Itami-Soil and Befu-Soil.

When to the mixture of superphosphate solution and bases or soils gelatine or peptone was added and, after having let it stand still overnight, the quantities of soluble phosphoric acid were determined by the molybdc method; they were always greater in the case of addition than without addition of gelatine or peptone. When greater quantities were added, the values of soluble phosphoric acid were greater, too. The favourable effects of gelatine were greater than those of peptone. As it has already been stated that when proteins such as gelatine and peptone were added to superphosphate solution, they kept the phosphoric acid soluble by physical adsorption and chemical combination, it could be naturally deduced that the same reactions would occur when to the mixture of superphosphate solution and bases or soils gelatine or peptone was added; and furthermore that gelatine or peptone would react with the added bases or the bases of added soils in the same way as with phosphoric acid. Therefore, in this case, the proteins would combine with and adsorb not only the phosphoric acid but also bases, accordingly the quantities of free phosphoric acid and of free bases

would decrease and the formation of insoluble substances caused by the reaction between them would be inhibited.

When the quantities of soils added to superphosphate solution or when the lengths of reaction time were increased the estimated values of phosphoric acid were gradually decreased. The effects of the different soils and those of added gelatine or peptone were entirely equal to those of the former experiments, they were the greatest with Toyama-Soil, followed by Itami-Soil and Befu-Soil, and the favourable effects of gelatine were greater than those of peptone.

In short, it was manifested that when lyophilic amphoteric colloid substances such as gelatine or peptone were added to superphosphate solution, the phosphoric acid was retained by the added substances through physical adsorption and chemical combination, at the same time that the bases added to superphosphate solution were also retained by the lyophilic amphoteric colloid substances through the same adsorption and combination, accordingly that the direct reactions between phosphoric acid and bases and the formation of insoluble substances between them were strongly inhibited. Thus the theoretical basis of manufacture of the author's non-retrograding superphosphate was established.

Chapter 4.

The effects of non-retrograding superphosphate upon the growth of plants.

In the former chapter, the results of experiments concerning the effects of lyophilic amphoteric colloid substances upon the phosphate ion of superphosphate solution were theoretically stated. By addition of lyophilic amphoteric colloid substances to superphosphate or its solution the retrogradation of calcium phosphate was surely inhibited. Thus the author was able to establish the theoretical basis of manufacture of non-retrograding superphosphate. However, for the purpose of practical application of non-retrograding superphosphate, it being also very important to know its effects upon the growths of plants, the author investigated the effects upon the growth of rice plant, as well as of wheat plant and also garden radish.

In the present chapter, the results of these experiments are to be described.

§ 1. Studies upon rice plant.

I. Preliminary pot experiments.

A. Soil. Collected from a grove of pine trees of Shinnobe, Befu Machi, Hyogo Prefecture, with the following chemical composition.

Table 23.

Chemical composition of the soil.

Moisture	1.01%
Loss on ignition	2.94
Humic substance	1.59
Hot HCl insoluble substances	92.40
Hot HCl soluble substances	
Iron oxide	0.93
Alumina	0.87
Phosphoric acid	0.14
Manganese oxide	0.12
Calcium oxide	0.22
Magnesia	0.83
Sulphuric acid (SO ₃)	0.97
Kali	0.09
Soda	0.11
Silica (SiO ₂)	0.76
Exchange acidity (KCl method)	6.30

B. Pots. 1/20000 Tan (1/40000 Acre) Wagner porcelain pots were used.

C. Fertilizer and its quantity supplied. The following fertilizers were supplied to each pot.

N. 1.44 g Supplied with 7.024 g ammonium sulphate of 20.5 % nitrogen.

P₂O₅ 1.44 g Supplied with 7.225 g superphosphate of 19.93 % water-soluble phosphate.

K₂O 0.960 g Supplied with 2.000 g kalium sulphate of 48 % K₂O.

The mixture of the three was called mixed manure. The lyophilic amphoteric colloid substance was made by mixing the same quantities of Merck peptone and White Bear Brand gelatine made in Germany. a) 5.4 % and b) 0.5 % lyophilic amphoteric colloid substances were added to the mixed fertilizer and c) nothing was added. These were

mixed with water and supplied to the soil as solutions. d) No manure was supplied.

D. Preparation of pots for cultivation. In each pot gravels were laid at a height of 6 cm, upon them pebbles, then 11.25 kg of the above soil were filled up.

E. Manuring period. One third of the quantities of the above mentioned fertilizer was given as a ground manure on June 23 1925, one third on July 15 and one third on July 24.

F. Plantation. On June 24 1925, one rice seedling of Akashiho of Asahi-Stock was planted in each pot.

G. Management. It was carried out according to the usual method.

H. On November 6 the plant was harvested.

I. Crops.

Table 24.
The crops of rice of pot cultivation.

	a	b	c	d
Height of plant (m)	0.976	0.967	0.942	0.858
Number of partitions of plant	58.6	43.0	32.3	14.6
Mean length of one ear(m)	0.136	0.165	0.172	0.160
Mean number of grains per one ear	50.7	57.3	66.1	58.9
Mean weight of unhulled rice per pot	83.6	70.6	47.9	26.9
Mean yield of rice hulls (g)	1.8	3.2	1.0	0.5
Mean yield of stalk per pot (g)	82.6	69.8	45.9	27.5
Mean yield of root per pot (g)	24.7	19.7	18.3	15.5

As the fertilizer were divided and given in three times, it was not without a suspicion of fitness for the investigation method to discuss the maintenance of solubility of phosphate. However, it was seen from the above table that the purpose of the present examination could be attained, thus the rice plants made better growths and more quantities of crops according to the addition of lyophilic amphoteric colloid substances and according as greater quantities of them were added.

It is the important problem of manure to prevent the change of phosphate into insoluble form and to devise the rational utilization

and the abridgment of manure. The quantities of phosphate absorbed and utilized by the crops were calculated as follows.

Table 25.
The contents, quantities and absorption coefficient of phosphate by crops.

	a	b	c	d
Grains	0.73%	0.69%	0.68%	0.67%
Stalks and rice hulls	0.34	0.32	0.30	0.14
Roots	0.55	0.53	0.51	0.43
Quantities of phosphate of crops	1.04 g	0.83 g	0.56 g	0.31 g
Absorption coefficient of phosphate	50.62%	36.11%	17.38%	—

By the above preliminary experiments it was seen that the absorption coefficient of phosphate ion of superphosphate became markedly higher by addition of lyophilic amphoteric colloid substances.

II. The regular experiments.

A. Studies on seedlings in seed-beds.

By the preliminary experiments, it was seen that the absorption coefficient of phosphate ion by rice plants became markedly higher by addition of lyophilic amphoteric colloid substances to the superphosphate solution. The author intended to investigate the effects of lyophilic amphoteric colloid substances which retained the phosphate ion of superphosphate solution by adsorption and combination, upon the growths of plants in the practical rice field.

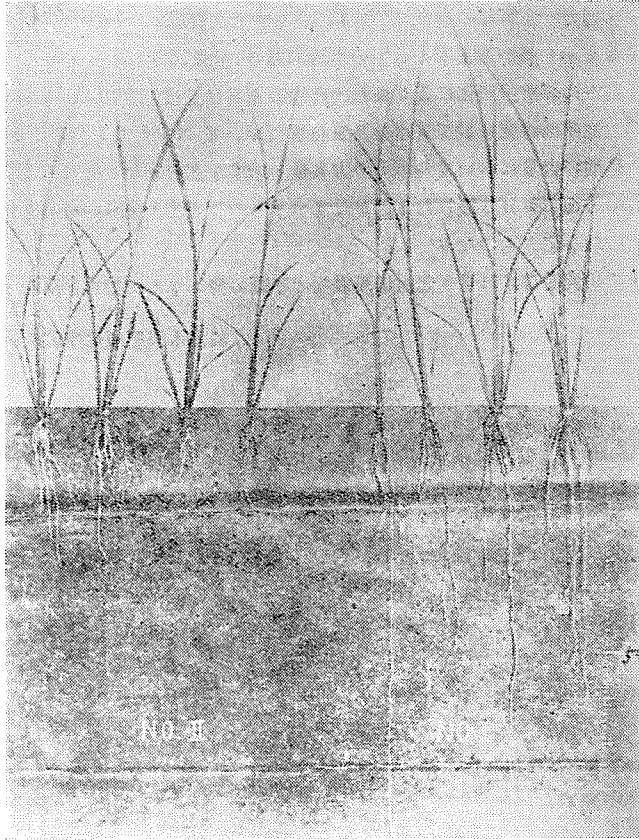
A manure contains soluble constituents available as nutrients for plants. However, they undergo many sorts of physico-chemical and biological changes and are partly lost in the soil. It goes without saying that a manure is added to soil not to increase a specific constituent, but to be used for the purpose of assimilation by the plant. For the accomplishment of this purpose, one must attend not only to the quantity, but also to the quality of the manure to be added. It can be said that the final object of manuring is to obtain the greatest quantities and the best quality of crops by the smallest quantity of manure.

The author, therefore, compared the effects of simple superphosphate and of non-retrograding superphosphate upon the growth of rice

Plate. 1

The appearance of rice seedlings.

(Collected on June 1 1925)



plant.

a. The preparation of seed-bed.

1. The arrangement of seed-bed.

A wooden box of 1.82 m × 1.36 m × 0.61 m (0.75 Tsubo) size, the inside of which was covered with iron plate so as to prevent the leakage of water, and at the bottom of which a drain of 0.1 × 0.1 m was prepared, and a draining hole and a watering tube were equipped, was buried in the field to the level of ground. Gravels of 0.02 m diameter were filled in the bottom of the box as one layer, then to the height of 0.15 m fine gravels and the sandy loam used in the preliminary experiment was laid upon them. Its quantity was 562.5 kg.

2. The preparation of manure.

i. Given quantities of superphosphate containing 19.5 % water-soluble phosphate and to it 10 % of a mixture of the same quantities of Witte peptone and White Bear Brand gelatine made in Germany were dissolved in water, mixed well, dried and powdered. Thus a non-retrograding superphosphate of 2.0 % total nitrogen and 19.07 % water-soluble phosphate was obtained. By addition of ammonium sulphate and the same superphosphate to the non-retrograding superphosphate a mixed manure of 8.0 % total nitrogen and 8.0 % water-soluble phosphate was prepared.

ii. A mixture of superphosphate and ammonium sulphate of 8.0 % total nitrogen and 8.0 % water-soluble phosphate was used as an inorganic mixed manure.

3. The quantities of manure and the manuring method.

124.0 g of each mixed manure were dissolved in water, after 24 hours the solution and after another 24 hours 280.0 g straw ash were given to each seed-bed. The seed-beds given the former organic mixed manure were called No. I and those given the latter inorganic mixed manure No. II.

4. The sowing.

On May 14 1928, manure was supplied, after one day the seed-bed was covered with water and 0.41 L (3 Go per Tsubo) seed rice of Akashiho of Asahi-Stock was sown.

b. The appearance of growth of rice seedling.

The appearance of growth of rice seedling No. I was inferior to that of No. II. The colour of the plant was always yellow green and

the plant was hard and tough to the touch in the case of No. I. In the case of No. II, the plant grew better, the colour was deep green, and the plant was soft to the touch. On the contrary, the development of root No. I was superior to that of No. II. On June 1, 70 plants each, on June 20, 150 plants and on June 25, 200 plants of each were collected. The lengths of stalks and roots were measured with the following results. The lengths of roots were measured only in the case of June 1, as the development of roots of the other two cases had been so flourishing, it was impossible to collect without injuring them.

Table 26.

The length of stalks and roots of rice seedlings at different times.

	June 1		June 20	June 25
	Stalks	Roots	Stalks	Stalks
No. I	0.246 m.	0.125 m	0.255 m	0.298 m
No. II	0.265	0.070	0.275	0.322

The development of roots No. I was flourishing. It can be said that by addition of lyophilic amphoteric colloid substances to superphosphate, the phosphate ion was adsorbed and held so as to supply soluble phosphate for a long time, and that, therefore, the development of roots was flourishing; that at the same time the supply of nitrogen was restricted, and the sound growth of rice seedling has resulted. On the contrary, in the case of No. II as the phosphate ion changed to insoluble form in soil solution, the effect of nitrogen was marked, and, accordingly, the luxuriant growth of stalks and leaves has resulted.

c. Observation of stalks and leaves.

To examine the changes of the constitution of stalks and leaves of the rice seedlings according to their development, on June 10, 20 and 25 100 g of rice seedlings of each group were collected, dried at 45°C for the first time, then at 65°C till constant weights were attained.

Table 27.

The weight of dry matter obtained from 100 g fresh rice seedlings of different stages of growths.

	June 10	June 20	June 25
No. I	20.61 g	24.04 g	22.08 g
No. II	19.78	22.90	20.18

The quantities of dry matters No. I were superior to those of No. II. Their analysis was carried out by the usual method with the following results.

Table 28.

The composition of dried rice seedlings of different stages of growths.
% of air-dry matter.

	June 10		June 20		June 25	
	No. I	No. II	No. I	No. II	No. I	No. II
Water	1.35	1.40	1.23	1.35	1.34	1.36
Total N	2.61	3.74	2.30	3.45	1.99	2.18
Protein N	2.42	3.28	2.20	3.17	1.64	1.79
Phosphoric acid	1.15	1.07	0.97	0.95	0.93	0.90
Pentosan	11.60	9.90	16.02	15.03	16.37	14.85

% of water free matter.

Total N	2.65	3.79	2.33	3.50	2.02	2.21
Protein N	2.45	3.33	2.23	3.21	1.66	1.82
Phosphoric acid	1.16	1.09	0.99	0.97	0.94	0.91
Pentosan	11.76	10.04	16.22	15.24	16.59	15.05

The contents of total nitrogen and protein nitrogen of No. II were superior to those of No. I, on the contrary, those of phosphate and pentosan of No. II were inferior to those of No. I. By addition of lyophilic amphoteric colloid substances, the phosphate retained its solubility for a long while and was markedly utilized by the plants. The pentosans are considered as an important material for the cell formation

in plant body. The rice seedlings No. I contained little nitrogen and much phosphate and pentosan, grew harder and tougher than No. II.

B. Studies of rice plants at rice field.

a. Cultivation and management.

1. Preparation of rice field. The rice beds used in the former experiments were used, the rice seedlings were removed, the earth ploughed, and prepared.

2. Fertilizers. Prepared in the same way as in the former experiment.

3. Quantities of fertilizer and its supply. The manure was supplied on July 28 1928. To No. I, 187.0 g manure i and 41.0 g K_2SO_4 were dissolved in water and used. To No. II, 187.0 g manure ii and 41.0 g K_2SO_4 were used in the same way. Both were supplied at once, no other fertilizer was supplied afterwards.

4. Planting. The strong rice seedlings grown in rice bed No. I were selected and planted at the intervals of 0.15 m.

5. Management. Water was poured on shallow; from time to time the rice field was dried spontaneously, weeds were removed occasionally. Pearl-moths were carefully exterminated. By means of a wire-netting, the plants were protected from injuries of birds.

b. Observations on the appearance of plant growth and of stalks and leaves.

The sprouting of new little roots after transplantation was earlier with No. I than with No. II. One month after transplantation, i. e. on August 1, the partitions of plant bodies were almost the same, the heights of No. I were inferior to those of No. II, but the developments of roots were contrary. These facts were observed not only in the author's experiment, but are general in the farmers' practical rice fields, when non-retrograding superphosphate was used, without regard to the climate and the soil.

The period from August 1 till September 13 was divided into seven terms; at each term plants were pulled out, and their heights were measured. The following Table 29 shows the measured mean values.

Table 29.
State of growth of rice plants.

	No. I	No. II
1st term Aug. 1	0.748 m	0.827 m
2nd term Aug. 9	0.887	0.910
3rd term Aug. 18	1.023	1.055
4th term Aug. 25	1.016	1.157
5th term Sept. 1	—	—
6th term Sept. 8	1.112	1.188
7th term Sept. 13	1.225	1.255
Coming of ears	Sept. 3	Sept. 6

After September 13 the plants bloomed. The heights of No. I were always shorter than those of No. II, the same was seen in the case of wheat, the statement of which will be found in the following chapter of this thesis. The coming out of ears of No. I was four days earlier than of No. II. The same fact was observed generally in all sorts of place, when non-retrograding superphosphate was used.

The stalks and leaves were treated in the same way as the rice seedlings. The following Table 30 shows the quantities of air-dried material of each rice plant.

Table 30.
Air-dried matters of rice plants at
the different stages of growth.

	No. I	No. II
1st term	17.47 g	15.81 g
2nd term	18.45	18.20
3rd term	21.99	20.97
4th term	24.31	22.32
5th term	23.60	21.80
6th term	26.67	26.20
7th term	28.63	25.92

The air-dried matters of No. I were always greater than of No.

II. The air-dried materials were analyzed by the ordinary methods with the following results.

Table 31.
The composition of air-dried materials
at the different stages of growth.

		Water	Total N	Protein N	Phosphoric acid	Pentosan
1st term	No. I	1.45	2.63	2.10	0.85	16.90
	No. II	1.42	2.95	2.27	0.81	16.02
2nd term	No. I	1.42	2.29	1.35	0.80	19.41
	No. II	1.37	2.33	1.70	0.72	18.94
3rd term	No. I	1.51	2.33	1.55	0.80	19.77
	No. II	1.47	2.65	1.85	0.78	18.36
4th term	No. I	1.46	1.65	1.38	0.69	20.70
	No. II	1.40	1.84	1.61	0.64	19.60
5th term	No. I	1.36	1.54	1.34	0.67	20.82
	No. II	1.43	1.90	1.55	0.62	19.85
6th term	No. I	1.40	1.53	1.31	0.64	18.97
	No. II	1.41	1.72	1.51	0.62	19.49
7th term	No. I	1.41	1.41	1.31	0.58	19.57
	No. II	1.40	1.78	1.61	0.57	18.55

Percentage of water-free matters.

		Total N	Protein N	Phosphoric acid	Pentosan
1st term	No. I	2.67	2.13	0.86	17.15
	No. II	2.99	2.30	0.82	16.26
2nd term	No. I	2.32	1.37	0.81	19.69
	No. II	2.36	1.72	0.73	19.20
3rd term	No. I	2.37	1.57	0.81	20.07
	No. II	2.69	1.88	0.79	18.63
4th term	No. I	1.67	1.40	0.70	21.01
	No. II	1.87	1.63	0.65	19.88

5th term	No. I	1.56	1.36	0.68	21.11
	No. II	1.93	1.57	0.63	20.14
6th term	No. I	1.55	1.33	0.65	19.24
	No. II	1.74	1.53	0.63	18.76
7th term	No. I	1.43	1.33	0.59	19.86
	No. II	1.81	1.63	0.58	18.81

These results were the same with those of rice seedling from the seed-beds. By addition of lyophilic amphoteric colloid substances, it was made clear that rice plants poor in contents of total nitrogen and protein nitrogen, rich in phosphoric acid and pentosans were obtained.

c. Harvest,

On November 1 1928, the rice plants were reaped, they were dried in a greenhouse for one month.

1. Preparing. The unhulled rice was obtained by threshing, and cleaned by means of a farming mill.

2. Weight and volume of unhulled rice. Under the same conditions, the following measurements were carried out. The figures are the mean values of ten measurements.

Table 32.

The grain numbers of 100 cc., weight and volume of 1000 grains.

	Grain number of 100 cc.	Weight	Volume
		of 1000 grains	
No. I	2081	30.62 g	48.05 cc.
No. II	2125	29.78	47.05

3. Hulling. By means of a hulling machine, the unpolished rice was obtained.

4. Physical examination.

Table 33.

The physical constants of the unpolished rice.

	No. I	No. II
Thickness of 1 grain (mean of 100 grains)	2.1404mm	2.0971 mm

Weight of 100 cc. (mean of 5 measurements)	Rough	87.900 g	86.160 g
	Tight	90.875 g	90.175 g
Grain number of 100 cc. (mean of 5 measurements)	Rough	3483	3552
	Tight	3579	3677
Weight of 1000 grains (mean of 5 measurements)		25.20 g	24.60 g
Hardness (mean of 1000 grains)	Breaking	6.7252 kg	5.8095 kg
	Crashing	8.8372 kg	8.6381 kg

It was seen that the quality of No. I was superior to No. II.
5. Chemical examination.

Table 34.
Chemical analysis of the unpolished rice.

	air-dried matter		water-free matter	
	No. I	No. II	No. I	No. II
Water	13.21%	14.52	—	—
Pentosan	6.29	5.96	7.25	6.87
Starch	69.35	66.50	78.89	77.80
Total N	1.06	1.16	1.22	1.36
Protein N	1.05	1.12	1.21	1.31
Phosphoric acid	0.65	0.62	0.75	0.72

Putting together the above results, the size of unhulled and unpolished rice of No. I was greater than of No. II, accordingly the grain number contained in a given volume was smaller by No. I than No. II, the weight and volume of No. I was superior to No. II. The thickness and hardness of unpolished rice No. I was superior to No. II. Regarding the chemical composition of unpolished rice, No. I was superior to No. II the contents of soluble carbohydrate such as pentosans and starch and phosphoric acid were greater in No. I than in No. II, those of total nitrogen and protein nitrogen were the inverse. It was made clear that when superphosphate had been supplied by addition of lyophilic amphoteric colloid substances, which resulted into a non-retrograding superphosphate, rice crops of superior quality as to physical and chemical property were obtained than when only untreated superph-

osphate had been supplied.

III. Remarks.

1. If the author considers the results obtained from the investigations on the rice plants, he comes to the following conclusions. When superphosphate was used as phosphate manure, it distributed throughout the soil, but changed gradually into compounds which were not utilized by the plants. When lyophilic amphoteric colloid substances were added to it, as has been cleared by the preliminary experiments, the solubility of phosphate was maintained, the absorption coefficient of phosphate by plants was remarkably raised, the utilization of phosphate was also raised.

2. The growth of rice seedling No. I was superior to that of No. II. The development of roots of rice plant No. I was superior to that of No. II. It could be said that the existence of soluble phosphate stimulated the development of roots of the rice seedling and a perfect growth of the rice plant was obtained.

3. As the absorption and the assimilation of phosphate were better, the heights of plant in No. I were shorter, the water contents were smaller, the pentosan contents were greater than those of No. II. Thus the healthy growth of the rice plants No. I was evident.

4. The early coming out of ears of No. I was an affair to be watched with care. As one reason of many reasons, it could be mentioned that the flourishing absorption and assimilation of phosphate hastened the maturity of the plants.

5. The size of unhulled and unpolished rice No. I was superior to that of No. II, the grain number of a given volume was contrary, the weight and volume of a given grain number of the former were superior to those of the latter. The thickness and hardness of unpolished rice No. I were superior to those of No. II. The contents of soluble and easily soluble carbohydrates such as pentosan and starch and that of phosphate were greater with No. I than with No. II and the contents of total nitrogen and protein nitrogen were contrary. It could be deduced that these phenomena were also due to the absorption and assimilation of phosphate by the plants.

§ 2. Studies upon the wheat plant.

The author investigated the absorption and assimilation by rice

plants of phosphoric acid of non-retrograding superphosphate manufactured by addition of lyophilic amphoteric colloid substances to superphosphate. Now, the results of wheat plants are described in this paragraph as follows.

I. Cultivation and treatment.

A. Cultivation. A part of the field was dug, framed by wooden case of $1.82 \times 1.82 \times 0.9$ m, the interior of the case was divided equally into two parts, the area of which was a half-Tsubo (ca. 1/2500 Acre). Seven hundred and fifty kg soil employed for the investigation of rice plants were added to each division.

B. Fertilizer. Two sorts of fertilizers employed in the investigation with rice plants were taken. They were a) mixed fertilizer containing colloid substances and b) anorganic mixed fertilizer.

C. Quantity and method of manuring. In the proportion of total nitrogen 15 kg, soluble phosphate 15 kg and soluble potash 11.25 kg per Tan (=ca. 1/4 Acre), 348.0 g of each mixed fertilizer and 39.0 g of potassium sulphate (K_2O 48 %) were supplied to each half-Tsubo. They were dissolved in water and completely distributed. The division supplied with fertilizer a) was called No. I and that supplied with b) was called No. II.

D. Variety. The employed wheat seed was Shinchunaga delivered from the Agricultural Society of Hyogo Prefecture.

E. Sowing. On November 6 1927, directly after manuring, sowing was carried out. In every half-Tsubo seventeen parallel ditches were prepared, to each ditch 60 grains were sowed.

F. Treatment. Cultivation, weeding, ridging etc. were performed as usual. Protections against diseases, insect and bird damages were performed with absolute security and thus treatment were completely performed.

G. Harvest. On July 3 1928, the crops were harvested at their complete ripeness.

II. Observations on the growth.

The sproutings of No. I and No. II were almost at the same time, but when four germ leaves had grown, an interesting morphological difference was already observed between both. The young plants of No. I hanged down their leaves against the ground at an angle of average 45° . Those of No. II, on the contrary, held their leaves upward

and the angle of their direction against the ground was average 60°. This morphological difference was recognized throughout the whole growing term. The growth of the root in No. I was wonderfully flourishing as compared with that of No. II.

For the preliminary observation of wheat growth, the young plants were gathered on January 3 and February 1 1928, at which time the length of the plants was about 15 cm. The materials were dried at first at 45°C, then at 60° until constant weight was obtained.

Table 35.

The weights of dry matter of young wheat plants.

	Original matter	Weights of dry matter of constant weight	Moisture
No. I	22.65 g	2.825 g	87.53%
No. II	22.975g	2.625 g	88.53%

The difference of 1.05 % moisture should be considered to be a factor of good or bad growth of the young plants. It was considered that the quantity of moisture given off had a direct connection with the cells' greater or smaller capacity of isolating their contents of moisture, and also with the density of consistence of the cell content. The weight of dry matter was higher in No. I than in No. II.

The nitrogen contents of these dried materials were measured according to the usual method with the following results.

Table 36.

The nitrogen contents of dry matter of young wheat plants.

	Water	Total nitrogen of	
		dry matter	water free matter
No. I	1.78 %	5.33 %	5.43 %
No. II	1.85	5.45	5.55

No. I contained smaller quantities of moisture and total nitrogen than No. II. This fact indicates that the nitrogen absorption was controlled by the phosphoric acid absorption, that the formation of carbohydrates was accelerated and so the good growth of the plants resulted. This was quite the same as in the case of rice plants.

For the purpose of observing the variations of compositions at different growth periods, the whole growing time, from four germ leaves till blooming time, was divided into eight periods, i. e. the 1st period 13 and 14 February, the 2nd 1 and 2 March, the 3rd 14 and 15 March, the 4th 30 and 31 March, the 5th 8 and 10 April, the 6th 19 and 20 April, the 7th 1 and 2 May and the 8th 10 and 11 May. At each period, samples were collected, dried and the quantities of dry matter were estimated as in the preliminary examination.

Table 37.

The weights of dry matter obtained from 100 fresh wheat plants of different stages of growth.

	No. I	No. II
1st period	16.04 g	15.31 g
2nd period	14.63	13.78
3rd period	16.99	15.76
4th period	16.74	15.84
5th period	16.83	14.53
6th period	18.90	18.58
7th period	26.85	22.55
8th period	34.90	32.66

No. I, seen from above, always surpassed No. II in the weight of dry matter. The dried materials were analysed by means of usual methods.

Table 38.

Composition of air dried materials at the different stages of growth.

		Water	Total N	Protein N	P ₂ O ₅	Pentosan
1st period	No. I	1.43%	5.04%	3.69%	2.55%	9.72%
	No. II	1.46	5.07	3.71	2.40	9.56
2nd period	No. I	1.32	4.49	3.19	1.76	11.26
	No. II	1.38	4.79	3.29	1.58	11.11

3rd period	No. I	1.36	3.46	2.79	1.79	12.86
	No. II	1.28	3.67	2.84	1.74	12.00
4th period	No. I	1.53	3.12	2.48	1.56	15.89
	No. II	1.49	3.37	2.69	1.47	15.10
5th period	No. I	1.40	3.03	2.44	1.18	18.98
	No. II	1.43	3.09	2.48	1.08	18.06
6th period	No. I	1.38	2.16	1.86	1.02	22.34
	No. II	1.40	2.37	1.97	1.01	19.65
7th period	No. I	1.36	1.68	1.46	0.88	19.32
	No. II	1.38	1.85	1.59	0.83	18.23
8th period	No. I	1.41	1.37	1.18	0.65	18.34
	No. II	1.40	1.53	1.33	0.54	18.02

Composition of water free materials.

1st period	No. I	5.11%	3.74%	2.58%	9.86%
	No. II	5.15	3.77	2.43	9.70
2nd period	No. I	4.55	3.23	1.78	11.41
	No. II	4.86	3.34	1.60	11.26
3rd period	No. I	3.51	2.83	1.82	13.04
	No. II	3.72	2.88	1.76	12.16
4th period	No. I	3.17	2.52	1.58	16.14
	No. II	3.42	2.73	1.50	15.33
5th period	No. I	3.07	2.48	1.20	19.25
	No. II	3.14	2.52	1.09	18.32
6th period	No. I	2.19	1.89	1.04	22.65
	No. II	2.40	2.00	1.03	19.93
7th period	No. I	1.70	1.48	0.89	19.59
	No. II	1.88	1.61	0.85	18.48
8th period	No. I	1.39	1.20	0.66	18.60
	No. II	1.55	1.35	0.55	18.28

The contents of total nitrogen and protein nitrogen of No. II

were always superior to those of No. I, and on the contrary, those of phosphoric acid and pentosan of No. I were superior to those of No. II. These relations were quite the same as in the case of rice plant examinations. It was to suppose that the wheat plants also had advanced the absorption and utilization of phosphoric acid by addition of lyophilic amphoteric colloid substances to superphosphate, and that the products poor in nitrogen compounds, rich in soluble and easily soluble carbohydrates resulted.

The difference of heights between both wheat plant at each growing period were measured with following results shown in the next table.

Table 39.

The heights of wheat plants at the different stages of growth.

	4th period	5th period	6th period	7th period	8th period
No. I	0.7920 m	0.9091 m	1.2870 m	1.2549 m	1.2549 m
No. II	0.8415	0.9900	1.3200	1.4190	1.3266

It was found from the table that the height growth of No. I was inferior to that of No. II. This was quite the same as in the case of rice plants and could be explained by the fact that the growth of No. I was reduced by excellent absorption and utilization of phosphoric acid.

III. Observations upon the crops.

The crops were harvested on July 9 1928. After separation of episperms, the seeds were dried in day light, the awns removed, and the seeds once more dried indoors for seven days and winnowed by wind. Several physical properties of the seeds selected by wind were determined.

The figures of the next table are averages of ten measurements.

Table 40.

The physical properties of the wind-selected seeds.

	Weight of	Volume of
	1000 grains	
No. I	31.521 g	39.50 cc.
No. II	27.221	35.19

It was found that No. I was distinctly far better both in weight and volume than No. II.

IV. Summary.

(1) In the examinations of wheat cultivation, similiary to those of rice, the contents of moisture and total nitrogen were lower in No. I, higher in No. II throughout the whole growing term. But the contents of phosphoric acid and pentosan were the reverse.

(2) This fact is to be carefully noticed not only in the cultivation of rice or wheat plants, but also in that of other useful plants. If one wishes an excellent quality and quantity of crops, he must cultivate first the stalks or leaves of plants as sound as possible. The employment of the author's non-retrograding superphosphate seems to be effective for attaining this purpose.

(3) As a result of a sound growth of stalks and leaves, in the case of wheat plants, the products of No. I were better in both weight and volume than those of No. II.

§ 3. Studies upon radishes.

The author has verified by the cultivation of rice and wheat plants that phosphoric acid was absorbed by plant more abundantly when lyophilic amphoteric colloid substances were added to superphosphate than in the case of ordinary superphosphate, and that there was a favourable effect upon plant growth when such colloid substances were added to superphosphate. The author intended to investigate also the influence of lyophilic amphoteric colloid substances upon the utilization of phosphoric acid by vegetables, when those substances were added to superphosphate. To this purpose were chosen radishes. In the harvest of 1929, radish was cultivated using the same fertilizers as supplied to rice and wheat plants (of the former chapters), and similar comparisons were carried out as stated below.

I. Cultivation and treatment.

A. Variety. Tenma radish.

B. Cultivation of field. The footpaths of 0.385 m width and 237.6 m length were prepared in the direction of south and north, the area of one footpath was 27.8 m².

C. Fertilizers. Fertilizers containing 6.0 % nitrogen, 6.0 % soluble phosphate and 6.0 % potassium was prepared by mixing ammonium

sulphate, superphosphate and potassium sulphate. A non-retrograding superphosphate was prepared by mixing one part of lyophilic amphoteric colloid substance, namely a mixture of equal quantities of gelatine and peptone and nine parts of superphosphate. The non-retrograding superphosphate thus obtained contained 2.9 % nitrogen and 29.97 % soluble phosphate. In No. II was used a mixture of three sorts of inorganic fertilizers mentioned above and in No. I was used non-retrograding superphosphate instead of superphosphate.

D. Time and quantity of manure. Twenty footpaths were prepared in the cultivated field on September 4 1929, and named the first No. I, the second No. II, the third No. I, the fourth No. II and so on. By such an exchanging method errors due to disproportion of soil quality could be avoided. Then 2.85 kg fertilizer were supplied to each foot-path.

E. Sowing. It was carried out on September 13 1929.

F. Treatment. After a few days the seeds germinated. When two germ leaves were found, some of the young plants were picked out, so that the intervals of the remaining young seedlings were 29 cm and their sizes were similar. For prevention of diseases an emulsion of pyrethrums was spread and this treatment was performed with an absolute security of success.

II. Observations upon the products.

A. Hardness. Radishes with similar weight and form were chosen for the test. Each sample was cut into round slices of 0.03 m thickness, as shown in figure, six points were set on the surface facing the root tip. Hardness was measured by an instrument designed by the author. The instrument was made of an iron disk of 0.0015 m thickness and 0.15 m diameter, in the center of the disk vertical iron pole of 0.0015 m diameter and 0.15 m length was attached. This pole, put in a glass tube, was allowed to move freely up and down. A beaker was placed on the disk and the point of the iron pole was set successively on each point of a radish slice. By gradual addition of small shot grains into the beaker, the pole penetrated into the slice when the weight of the small shot overcame the maximum resistance of the radish tissue. The hardness of radishes was indicated by the weight of the small shot grain at that time. The mean value of six tests (on the six marked points) was taken as the hardness of the same bit. From some large radishes even seven bits were taken. The mean hardness of one radish

Fig. 1

Indicating the points set on the surface of a radish slice.

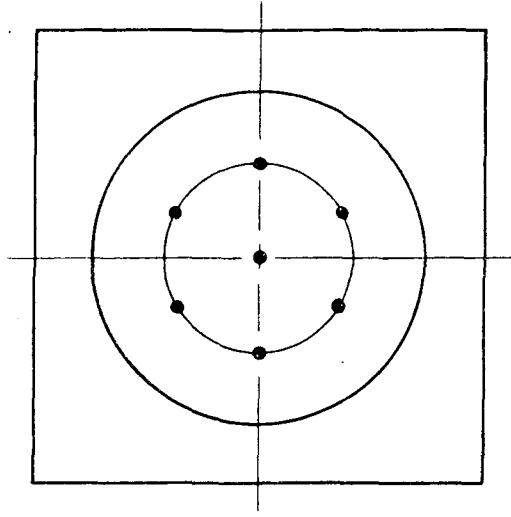
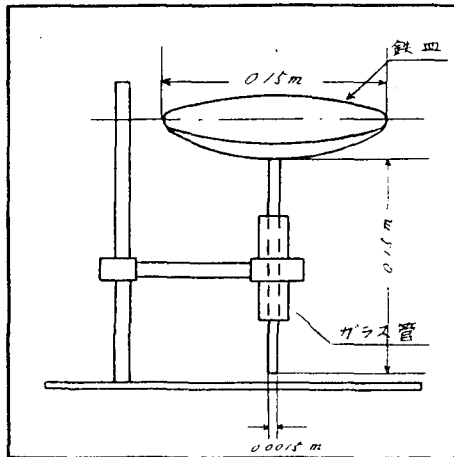


Fig. 2

The instrument of measuring hardness, designed by the author.



was an average of the mean values of all its bits. The results are shown in the following Table 41.

Table 41.
The weight, length, diameter and hardness
of radishes of different stages of growth.

	Weight (g)		Length (cm)		Mean diameter (cm)		Mean hardness	
	No. I	No. II	No. I	No. II	No. I	No. II	No. I	No. II
1st, Nov. 22	524.0	551.0	24.0	22.7	17.9	18.8	1756.0	2055.0
2nd, Nov. 29	732.0	708.5	25.3	28.5	20.4	19.8	1568.5	2065.1
3rd, Nov. 30	375.0	396.0	19.4	21.0	17.1	16.4	1860.2	2101.1
4th, Dec. 4	655.5	735.5	25.7	23.7	19.6	21.4	1909.7	1848.0
5th, Dec. 5	689.0	695.0	24.4	26.4	20.3	22.1	1711.7	1786.5
6th, Dec. 6	494.0	511.0	21.4	19.9	18.4	19.9	1948.6	2111.6
7th, Dec. 7 am	570.0	564.5	18.7	17.6	21.4	22.0	1843.8	1855.8
8th, Dec. 7 pm	646.0	523.0	19.1	16.7	22.4	22.1	1564.4	2108.9
9th, Dec. 10	505.0	556.0	20.8	20.8	19.9	19.5	1960.6	2102.7
10th, Dec. 11	491.0	463.0	22.7	22.8	17.5	17.6	1652.9	1944.9
11th, Dec. 13	478.0	495.0	16.7	18.3	20.9	20.7	1867.3	1190.9
12th, Dec. 14	496.0	599.0	20.6	20.4	19.2	20.4	2259.1	2263.7
13th, Dec. 18	476.5	403.0	20.7	19.1	17.7	17.5	1689.4	2075.5
14th, Dec. 20	471.0	551.0	18.3	18.5	19.5	20.8	1962.6	2146.0

During one month, from November 22 until December 20, measurements of hardness of radish were carried out. According to the Table, it was found that No. I was far softer than No. II. It is to be supposed that such a soft radish is of fine quality and contains plenty of soluble and easily soluble carbohydrates and less fiber; and that the hard radish is of rough quality contains plenty of fibre and less soluble and easily soluble carbohydrates.

B. Investigation of juice.

The radishes of similar weight, length and thickness were smashed and pressed by means of a ceramic press. The pressed juice was filtered. The filtrate was centrifuged for 10 minutes at 3000 rotations per minute. The specific gravity of the clear juices was measured by a pycn-

ometer, its surface tension by Du Nouy's tensiometer, its pH value by electrometric method, its reducing sugars by Bertrand method, its phosphoric acid by usual method, its total nitrogen by Kjeldahl method, its protein nitrogen by Stutzer method and its free amino nitrogen by Van Slyke's apparatus. The results were as follows.

Table 42.
The analyses of the radish juice.

		Specific gravity	Surface tension dyne/cm	pH	Contained in 100 cc. juice				
					Reducing sugar	Phosphoric acid	Total nitrogen	Protein nitrogen	Free amino nitrogen
1st, Nov. 25	No. I	1.0225 (15°C)	53.5 (18°C)	4.71	2.7385 g	72.09mg	73.92mg	39.42mg	—
	No. II	1.0225 (15°C)	52.2 (18°C)	5.03	1.4530	84.84	99.79	49.28	—
2nd, Nov. 29	No. I	1.0235 (19°C)	—	4.73	2.1510	65.97	70.22	44.35	—
	No. II	1.0225 (19°C)	—	4.34	2.1040	69.53	98.56	46.82	—
3rd, Nov. 30	No. I	1.0250 (18°C)	56.3 (18°C)	4.38	2.2765	79.33	77.62	36.96	33.21mg
	No. II	1.0235 (18°C)	55.6 (18°C)	4.83	2.5050	76.55	78.85	39.42	29.77
4th, Dec. 4	No. I	1.0225 (18°C)	55.9 (17°C)	3.68	2.6155	77.83	66.53	32.03	31.26
	No. II	1.0225 (18°C)	54.2 (17°C)	3.75	2.2630	63.79	81.31	39.42	32.42
5th, Dec. 5	No. I	1.0225 (17°C)	58.2 (17°C)	3.29	2.6165	75.27	75.15	34.49	24.02
	No. II	1.0225 (17°C)	56.6 (17°C)	3.45	2.4725	66.35	78.85	41.88	20.59
6th, Dec. 7	No. I	1.0240 (16°C)	55.2 (15°C)	2.75	2.7510	73.99	66.88	34.46	33.90
	No. II	1.0225 (16°C)	54.9 (15°C)	2.88	2.0510	92.49	73.92	39.42	38.14
7th, Dec. 10	No. I	1.0250 (17°C)	57.3 (17°C)	3.18	2.5857	80.38	92.40	41.89	40.91
	No. II	1.0225 (17°C)	55.9 (17°C)	3.88	2.5582	72.08	66.53	32.03	21.96
8th, Dec. 11	No. I	1.0225 (17°C)	56.3 (17°C)	3.62	2.1630	87.39	61.60	35.48	34.77
	No. II	1.0250 (17°C)	55.9 (17°C)	3.74	2.3855	86.21	62.83	36.96	23.34
9th, Dec. 13	No. I	1.0250 (20°C)	57.3 (17°C)	2.62	2.1898	95.69	76.38	36.96	30.55
	No. II	1.0250 (20°C)	55.5 (17°C)	3.23	2.3610	79.74	89.93	41.89	28.53
10th, Dec. 14	No. I	1.0250 (20°C)	55.9 (17°C)	4.23	2.5890	77.83	72.69	36.96	34.74
	No. II	1.0250 (20°C)	55.2 (17°C)	4.98	2.5639	75.27	75.15	29.57	18.53
11th, Dec. 17	No. I	1.0235 (20°C)	55.9 (17°C)	4.16	2.5025	96.96	75.15	22.18	44.23
	No. II	1.0225 (20°C)	55.2 (17°C)	5.15	2.4423	91.24	76.38	34.49	26.77

12th, Dec. 18	No. I	1.0250 (19°C)	55.9 (17°C)	4.28	2.5030	96.96	64.48	24.64	39.20
	No. II	1.0225 (19°C)	55.6 (17°C)	5.56	1.6445	89.31	77.19	29.57	33.39
13th, Dec. 20	No. I	1.0250 (17°C)	56.3 (17°C)	4.27	2.5259	109.08	81.93	32.53	41.51
	No. II	1.0225 (17°C)	55.9 (17°C)	5.31	2.3597	101.43	68.22	21.57	23.02

As seen from the table, there was a tendency of higher specific gravity in No. I than in No. II. As to surface tension, No. I was always higher, and it was deduced accordingly that the contents of surface active substances were higher in No. II than in No. I. About pH value, No. I was lower than No. II. Reducing sugars were contained more in No. I than in No. II except the 3rd, 8th and 9th periods. As regards phosphoric acid content, No. II was higher in the beginning of the examinations, but at last No. I had a tendency of containing higher phosphoric acid content than No. II. For this reason, it was considered that phosphoric acid changed slowly to effective form in No. I by addition of lyophilic amphoteric colloid substances. The total nitrogen and protein nitrogen were higher in No. II than in No. I. These were quite the same results with former investigations of rice and wheat plants. Free amino nitrogen was contained more in No. I, accordingly it was considered that the free amino acids contents were also higher in No. I than in No. II. And this fact would be one of the reasons why the pH value of No. I lay on the acidic side.

III. Summary.

(1) As regards the hardness, it was lower in No. I than in No. II. Therefore, the quality of the former was softer than that of No. II.

(2) The specific gravity and quantity of reducing sugars of juice tended to be high in No. I. Accordingly it was supposed that No. I had a better quality of cell contents.

(3) The higher contents of phosphoric acid particularly in No. I were a matter, of course, due to the influences of superphosphate to which lyophilic amphoteric colloid substances were added. Consequently, it was supposed that by this addition the vital function of radishes received favourable impulse, which resulted in the good quality of No. I.

(4) The higher contents of total nitrogen and protein nitrogen

of the juice of No. II would manifest that the nitrogen was in an easily absorbable and assimilable condition. The pH value of juice was higher in No. II. The reason for which would be that the quantities of phosphoric acid and free amino nitrogen, accordingly the free amino acids of No. I were higher than those of No. II.

§ 4. Discussion.

The cultivations of rice plants, wheat plants and radishes were carried out by the use of two sorts of superphosphates as source of phosphoric acid, one of which was a non-retrograding superphosphate with added gelatine and peptone, and the other a simple superphosphate without any addition. The growths of plants of the former case were superior to those of the latter case. Besides, the absorption coefficients of phosphoric acid were high, the yields of the products were great and the qualities of the products were excellent. Accordingly, the experiment was able to prove positively that the author's non-retrograding superphosphate is a particularly excellent phosphoric manure for plant growth.

As explained already in former chapters, when such lyophilic amphoteric colloid substances as gelatine and peptone were added to the superphosphate, these colloid substances held phosphoric acid and other constituents of superphosphate through physical adsorption or chemical combination. When various bases or soils were mixed with them, the lyophilic amphoteric colloid substances held the bases through physical adsorption or chemical combination. Therefore, the precipitation of phosphoric acid by reactions between phosphate ion and these various bases, namely the formation of insoluble phosphates was markedly inhibited. In other words, the lyophilic amphoteric colloid substances protected strongly the phosphoric acid from retrogradation rendering it insoluble.

Two sorts of phosphoric acids were used in the cultivation of plants described in these chapters. One of which had its phosphoric acid protected through adsorption and combination by lyophilic amphoteric colloid substances, and the other received no such protection. In the soil, the latter changed into hardly or scarcely utilizable form on account of gradually varying to insoluble. The former, however, remained soluble in soil for a long time as compared with the latter.

Therefore, it was evident that the plants easily and abundantly utilized it.

The following reasons may account for it. The adsorption and combination between proteins and phosphoric acid may be feeble. The plants may decompose the combined substances in soil, let phosphoric acid free, then absorb and utilize the free phosphoric acid produced. Generally proteins are easily decomposed by the action of micro-organisms and produce various decomposition products. Accordingly the protein part of a protein-phosphoric acid-complex is gradually decomposed by micro-organisms in soil, the phosphoric acid which is adsorbed and combined becomes free, and the plants are able to absorb and utilize it at once. In a word, the phosphoric acid of the non-retrograding superphosphate, i. e. the protein-phosphoric acid-complex supplied to soil is easily absorbed and utilized by plant roots. At the same time, the protein part of the non-retrograding superphosphate is decomposed by soil micro-organisms, and the free phosphoric acid thus produced is absorbed, assimilated and utilized by plants. The crops when supplied the non-retrograding superphosphate held the source of phosphoric acid for a long time, consequently achieved flourishing growth and bore successfully. It was to be inferred that by this reason the crops under effect of non-retrograding superphosphate yielded better results as compared with the case supplied with simple superphosphate.

Chapter 5.

Conclusion.

1. Studies on superphosphate were carried out since the beginning of the 19th Century and many investigators have reported on its properties and its utilization as fertilizer. However, studies concerning how one was able to inhibit its changes during its storage and how one was able to raise its availability by plants by means of excluding many reactions between superphosphate and soil constituents are very scarce. Accordingly, the author had intended to obtain a non-retrograding superphosphate by addition of lyophilic amphoteric colloid substances to superphosphate. He has studied the product theoretically, also the changes during its storage and its effects upon plant growth. Thus more than 30 years have already elapsed since he engaged himself in

these studies. In the present work, the author has collected and reported his results as already stated in the former chapters.

2. A superphosphate was manufactured on November 16 1936 using a mixed rock phosphate of 3.04 % content of iron oxide and alumina. To a part of superphosphate thus obtained were mixed lyophilic amphoteric colloid substances. Both sorts of superphosphates were stored until April 1941. By the analyses during the time, it was observed that the former had markedly retrograded to insoluble form, while the latter had scarcely retrograded.

3. When lyophilic amphoteric colloid substances were added to superphosphate solution, the phosphate ion was adsorbed, combined and retained by the added colloid substances, the electrical conductivity of the outer solution by dialysis had decreased, and the effects were proportional to the quantities of the added colloid substances.

4. The quantities of dialysable phosphate ion were decreased by addition of lyophilic amphoteric colloid substances and, the more the added colloid substances, the greater was the depression.

5. The superphosphate solution decreased its saccharose inverting power by addition of lyophilic amphoteric colloid substances. As the power was said to be in proportional relation with the free hydrogen ion concentration of the solution, it could be deduced that the hydrogen ion concentration of superphosphate solution was diminished by the addition, and also that lyophilic amphoteric colloid substances had adsorbed, combined and retained not only the anions but also the cations of the solution.

6. The chemical reactions between the phosphate ion of superphosphate solution and CaO , MgO , $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, or soils of different compositions were retarded markedly by addition of lyophilic amphoteric colloid substances. The effects of the colloid substances were in proportional relation to their quantities, and the more their quantities, the more was the inhibition of retrogradation to insoluble form of the phosphate ion.

7. When the effects of lyophilic amphoteric colloid substances to superphosphate solution were examined by taking the quantities of soils added to superphosphate solution or the lengths of reaction time in consideration, it was always observed that the added colloid substances had a marked significance upon the inhibition of retrogradation

to insoluble form of superphosphate. It was clearly verified that the colloid substances had adsorbed, combined and retained the phosphate ion without regard to the class of soils. It was, therefore, justified to say that the phosphate ion was strongly protected from retrogradation by the added colloid substances.

8. In short, the following facts were manifested that when lyophilic amphoteric colloid substances such as gelatine or peptone were added to superphosphate solution, the phosphoric acid was retained by the added substances through physical adsorption and chemical combination, at the same time that bases added to superphosphate solution were also retained by lyophilic amphoteric colloid substances through the same adsorption and combination, accordingly that the direct reaction between phosphoric acid and bases and the formation of insoluble substances between them were strongly inhibited. Thus the theoretical basis of the manufacture of the author's non-retrograding superphosphate can be regarded as established.

9. The effects of phosphate ions of both kinds, namely those of superphosphate prepared by addition of lyophilic amphoteric colloid substances and that of superphosphate without such annexes, to plant growth were compared and reported.

The experimental divisions to which the former superphosphate was supplied were called No. I and those to which the latter superphosphate was supplied was called No. II.

10. By pot experiments of rice plants, the absorption coefficient of phosphate ion of No. I was markedly higher than that of No. II.

11. In the cases of rice plants and wheat plants, the development of roots No. I was flourishing. One was able to say that the phosphate ion stimulated the roots of seedlings, and accordingly the roots developed actively. As long as the development of roots was flourishing, the development of leaves and stalk seemed to be inhibited, in this respect that of No. I was inferior to that of No. II. The number of tillerings of No. I was smaller than that of No. II, the colour of No. II was deep green, while that of No. I was always yellow green.

12. According to the chemical analyses of rice plants and wheat plants, the water content and the nitrogen content were greater in No. II. Therefore, it was seen that the greater the water content, the nitrogen content was also greater and vice versa, and that both were

in a closed relation.

13. The contents of phosphoric acid and pentosan of No. I were greater than those of No. II.

14. When superphosphate was supplied, the greater part of phosphoric acid was changed insoluble and fixed by soil, and only the smaller part was utilized by plants. However, it was the contrary in the case of non-retrograding superphosphate.

When nitrogen, phosphoric acid and potash were supplied, in the former case, the plant growths were influenced mainly by nitrogen and potash, the effect of phosphoric acid was faint, the colour of leaves was deep green, the number of tillerings was great. These phenomena are generally considered as advantageous, but the facts are contrary. The water content and the nitrogen content were great, the tissues were loose and soft, the plants were apt to suffer from injuries of diseases and insects, the crops were not so many. In the latter case, the absorption coefficient of phosphoric acid was high, the colour of leaves was yellow green, the number of tillerings was small. However, the water content and the nitrogen content were small, the pentosan content was great, the tissues were hard and strong, the plants were markedly resistant to injuries of diseases and insects, the crops were excellent and abundant.

15. Rosa and Hooker (10) suggested that pentosans caused winter hardness because they were highly colloidal chemical compounds which had enormous water-holding capacity. The results described above coincided very well with this suggestion. By the marked utilization of phosphoric acid by plants, a greater pentosan content is able to be expected. It is believed that the winter withering of plant can be reduced to no little extent.

16. The physical and chemical properties of the crops of No. I were always superior to those of No. II.

17. Concerning radishes, the quality of No. I was softer than that of No. II, the specific gravity, the quantity of reducing sugars, the contents of phosphoric acid and free amino nitrogen of juice of No. I were greater than those of No. II, and the contents of total nitrogen and protein nitrogen were the reverse. The pH value of juice was higher in No. II. Accordingly it was supposed that No. I had more excellent quality than No. II.

18. The following inferences may be deduced from the experimental cultivations of rice plants, wheat plants and radishes. When non-retrograding superphosphate, namely a protein-phosphoric acid-complex is supplied to soil, its phosphoric acid is easily absorbed by the plant roots and at the same time its protein part is decomposed by soil micro-organisms, the free phosphoric acid thus produced is absorbed, assimilated and utilized by plants. The crops when supplied with non-retrograding superphosphate hold the source of phosphoric acid for a long time, consequently achieved flourishing growths and bear successfully. It is to believe that by this reason the crops supplied with non-retrograding superphosphate yield better results as compared with those supplied with simple superphosphate-

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