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THESIS

DEVELOPMENT OF SUSPENSION FERTILIZER PRODUCTION WITH SOLID RAW MATERIALS

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A Thesis Submitted in Partial Fulfillment of
the Requirements for the Degree of
Doctor of Philosophy (Agricultural Research and Development)
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The objectives were to research a new suspension fertilizer process by using solid raw materials instead of liquid raw materials. The research was consisted of 5 experiments. The experiment 1 was aimed to investigate the effects of particle sizes of solid raw materials and speeds of agitator on the solubility of each solid raw material. The experiment 2 was conducted to investigate the effects of temperatures of solution and concentrations of suspending agent on the production of 25-7-7 suspension fertilizer. The experiment 3 was conducted to investigate the effects of stored periods on physical properties of 25-7-7 suspension fertilizers. The experiment 4 was conducted to investigate the effects of stored periods and the various suspension fertilizer grades on chemical and physical properties. The processes were to add 72.1 g Urea 1 in the first stage, simultaneously, 6.6 g xanthan gum, 9.1 g KCl, 29.7 g MKP and 47.5 g Urea 2 in the second stage, respectively, into the cylindrical glass bottle which was mounted to the adjustable speeds and presented 55.0 g of water. The obtained fertilizer was evaluated in chemical and physical properties: N, P_2O_5, K_2O, pH, specific gravity, viscosity, stability, pour-ability and salting out. The experiment 5 was conducted to investigate efficiency in use of 25-7-7 suspension fertilizer on plant growth and yield of Chinese kale. The experiments showed results in Luxen's method that was consisted of 4 factors: 1) particle size of solid raw materials of > 20 meshes, 2) speeds of agitator of 1820 and 2620 rpm, 3) temperature of solution of 30-40°C and 4) suspending agent of xanthan gum. It was the new suspension fertilizer production method that could process various suspension fertilizer grades with both the appropriate chemical and physical properties.

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Student's signature Thesis Advisor's signature

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Pichai Triratanaprapunta

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DEVELOPMENT OF SUSPENSION FERTILIZER PRODUCTION WITH SOLID RAW MATERIALS

INTRODUCTION

Nowadays, most of the suspension fertilizer plants use liquid raw materials as the sources of nitrogen, anhydrous NH_3 (82% N), aqueous NH_3 (20% N), sources of phosphorous, ortho phosphoric acid (wet process acid, 55% P_2O_5), super phosphoric acid (wet process acid, 75% P_2O_5) and solid mono ammonium phosphate (MAP: 12-60-0), source of potash, KCl (60% K_2O) and sources of suspending agents, clay, bentonite and gum, for the suspension fertilizer production method (Achorn and Hargett, 1980). Thereby, the liquid starters for formulating suspension fertilizers, which are both NP base suspension fertilizers such as 8-24-0 (Wilbanks, 1967), 10-30-0 (Getsinger et. al., 1984), 9-32-0 (Mann *et. al.*, 1983), 10-34-0, 12-40-0, 12-36-0 with ammonium lignosulfonate (Byrd and Scott, 1979; Jones, 1978; Striplin Jr *et al.*, 1962; Burnell and Rylant, 1990) and urea-ammonium nitrate solution (UAN): 28-0-0, 30-0-0 and 32-0-0 (International Plant Nutrition Institute, 2012) are obtained**.** The other methods are simultaneously used the fluorosilicic acid and suspending agents: clay for inhibiting large crystals formation of mono ammonium phosphate in the suspension fertilizer such as 12-12-12 (Mills, 1962), 14-14-14, 20-10-10 and 24-8-8 (Jones and Stinson, 1983; Dillard and Burnell, 1991), 11-39-0 (Wilbanks and Faulkner, 1980). Some methods are comprised the reaction product of urea, sulfuric acid and phosphoric acid for the production of 20-20-0, 10-37-0, 5-45-0 (Stoller and Hartung, 1982), 29-0-0-5S (Tennessee Valley Authority: TVA, 1985) and etc.

All of them which are produced in the conventional suspension fertilizer plants are based on hot mix process of the TVA three-stage continuous ammoniated type. The acid is ammoniated in three stages, with precise control of temperature and pH in each stage (Jones and Getsinger, 1979). When the ortho phosphoric acids are fed into the tank reactor (also pipe reactor) through a connecting pipe, anhydrous NH_3 and potassium salt are subsequently fed into them through another connecting pipe. The reaction occurred under high temperature which is more than 350^0C and high

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pressure. Thereby, there might be a risk of a massive explosion at the fertilizer plant where this process is used. This kind of serious accident had killed as many as 15 people and injured more than 160 in April, 2013, in the West Texas. The explosion left large damaged areas and more than 150 buildings damaged. The disaster was not the first time but was the sixtieth time since 1953 (Lateef, 2013).

Moreover, the conventional plants are extensively complicated in the handling of liquid raw materials in many tanks and cooling tower with corrosive condition. It is also complicated to produce the UAN (urea ammonium nitrate) solutions because of the ammonium nitrate operation with explosive material and it is strictly controlled by Thai Ministry of Defense. The production process is required high maintenance and high investment cost. Under Thailand condition, the suspension fertilizer production using solid raw materials is a possible alternative. The appropriate suspension fertilizers are consisted of pH 7.5-8 (Miller, 1962), fairly low viscosity, long term storage stability, no settlement, stable rheological behavior, easily pourable and low rate of crystal growth (Leikam, 2008; Frangioni *et. al*., 1976). The factors that may affect on the appropriate suspension fertilizer production are the usage of suitable milled solid raw materials, speeds of agitator and temperature of solution for achieving the saturated solution stage. In the suspension stage, the addition of suitable concentration of suspending agents and speed of agitator are employed for the appropriate suspension production. Present knowhow in solving those concerned factors is not enough to produce a good suspension fertilizer in high efficiency. Xanthan gum is the appropriate suspending agent because of its dissolving ability in both hot and cold water, exhibiting high viscosity at a low concentration, maintaining its viscosity in high ionic environments, and very low viscosity at high shear rates (Milas *et al*., 1985), Moreover, in the presence of salt it is insensitive to pH over the range pH 2-10 and having no trace elements such as Fe, Ca, Mg, Al (Sandford *et al.,* 1977). However, the knowledge for its use in suspension fertilizer production through solid raw materials has been less known, since the process is not thoroughly investigated in the past. Therefore, present research effort was to investigate for the first time those factors effecting the suspension fertilizer production using solid raw materials.

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The main objective of this research was to obtain an improvement of suspension fertilizer production method using solid raw materials instead of liquid raw materials. Xanthan gum was used in the production for obtaining the appropriate suspension fertilizers with good in both chemical and physical properties. A general and suitable fertilizer for both foliar application and fertigation, the 25-7-7 analysis grade of suspension fertilizer, is the target of this investigation.

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OBJECTIVES

1. To improve the suspension fertilizer production method

2. To obtain the desired analysis grades of suspension fertilizers with their chemical and physical properties

3. Fertilizer use Efficiency

4. Fertilizer cost of suspension fertilizers

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LITERATURE REVIEW

Fertilizers are products that to improve the levels of available plant nutrients and/or the chemical and physical properties of soil, thereby directly or indirectly enhancing plant growth, yield, and quality. They are any organic or inorganic material of natural or synthetic origin (other than liming materials) (Soil Science Society of America, 2012).

A recent assessment found that about 40 to 60% of crop yields are attributable to commercial fertilizer use (Stewart *et al*., 2005). They are essential for high-yield harvest: European fertilizer market is expected to grow to €15.3 billion by 2018 (Ceresana, 2012). Mined inorganic fertilizers have been used for many centuries, whereas chemically synthesized inorganic fertilizers were only widely developed during the industrial revolution. Increased understanding and use of fertilizers were important parts of the pre-industrial British Agricultural Revolution and the industrial Green Revolution of the 20th century. Inorganic fertilizer use has also significantly supported global population growth. It has been estimated that almost half the people on the Earth are currently fed as a result of synthetic nitrogen fertilizer use (Erisman *et. al*., 2008).

Fertilizers typically provide, in varying proportions:

1. Six macronutrients: nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), and sulfur (S)

2. Eight micronutrients: boron (B), chlorine (Cl), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), zinc (Zn) and nickel (Ni)

The macronutrients are consumed in larger quantities and are present in plant tissue in quantities from 0.15% to 6.0% on a dry matter (0% moisture) basis (DM). Micronutrients are consumed in smaller quantities and are present in plant tissue on

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the order of parts per million (ppm), ranging from 0.15 to 400 ppm DM, or less than 0.04% DM (AESL, 2010; Mills and Jones, 1996).

Only three other macronutrients are required by all plants: carbon, hydrogen, and oxygen. These nutrients are supplied by water and carbon dioxide.

The nitrogen-rich fertilizer ammonium nitrate is also used as an oxidizing agent in improvised explosive devices, sometimes called fertilizer bombs, leading to sale regulations (U.S. Department of Homeland Security, 2012).

Types of fertilizers are available in the market (UNIDO/IFDC, 1998).

1. Straight fertilizers supply single plant nutrient either nitrogen (N), or phosphorus (P), or potassium (K). Example: urea supplies 46% N; Super phosphate provides 7% P or 16% P_2O_5.

2. Compound fertilizers supply more than one plant nutrient. Example: Di-Ammonium Phosphate (DAP) contains 18% N and 20% P (46% P_2O_5).

3. Mixed fertilizers are physical mixture of two or more straight and/or compound fertilizers to supply particular combination of plant nutrients. Example: one can buy DAP and Muriate of Potash and mix them in a ratio to get a fertilizer mixture containing a grade of 12-32-16 of N, P_2O_5, and K_2O.

Types of fertilizers are divided into 2 groups based on physical property.

1. Solid fertilizers supply one or more than one plant nutrient in solid form including crystal and powder: straight fertilizers, complex fertilizers and mixed or compound fertilizers.

2. Liquid or fluid fertilizers supply one or more than one plant nutrient in

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liquid form: clear liquid mixed fertilizers, suspension fertilizers, slurry fertilizers and liquid ammonia: UAN (32-0-0), 10-34-0, and 11-37-0.

Liquid or fluid fertilizer

Liquid or fluid fertilizers were usually used in fertigation system could be divided into 2 types (Osothsapa, 1993).

1. Clear liquid mixed fertilizers (solution fertilizers): they are free of solids in which contain one or more than one plant nutrient that are dissolved completely in the solution, such as 12-6-6, 9-9-9, UAN (32-0-0) and 10-34-0. Solution fertilizers are low in potash because no more than 11 percent potash will go into solution, and 9 percent is more practical to manufacture.

2. Suspension fertilizer: plant nutrients are partially dissolved in the solution, but some of the nutrients, particularly potash, are suspended in the solution by suspending agent. It contains at least one of N, P, and K in prearranged ratios for various agricultural applications. Normally Suspension fertilizers contain greater than 9 percent potash in solution, such as 15-5-20, 15-15-15, 20-4-16, 18-18-18 and 7-13-34.

Liquid fertilizers are popular because of the ease of handling and use. Movement is by pump, and they usually require less labor to handle. Some pesticides can be injected into the fluid, saving trips across the field. Properly applied, particularly fertigation system, fluid fertilizers are no more or less efficient than conventional fertilizers. Most fluid fertilizers contain the same basic ingredients as conventional fertilizers. The only difference is that fluid fertilizers are dissolved in water, and conventional (granular) fertilizers are not (Table 2). The efficiency of fluid fertilizers is determined by the way they are applied.

The first time in 1962, Thailand imported clear liquid mixed fertilizers for use in orchids only. Later, they were used in other crops such as field crops, vegetables

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and fruit crops as a supplement application by foliar spraying. At the same time, the conventional fertilizers were used in mainly application (Osothsapa, 1993). At present farmers usually use foliar fertilizers which are solid or powder phase instead of clear liquid mixed fertilizers and use the conventional fertilizers in mainly application as well. Some farmers apply more plant nutrients essential to crops in fertigation system by using granular fertilizers which are dissolved with water, fillers are filtered off, and then plant nutrients in clear solution are irrigated. It is not propriety because they are desired for sowing or broadcasting in use. But the clear liquid mixed fertilizers, particularly suspension fertilizers, are unavailable in markets, the knowledge of them are difficultly to find out also. Suspension fertilizers are suitable for fertigation system (**Table 1 and 2**).

Table 1 Comparison in physicals and chemicals properties between solution fertilizer and suspension fertilizer

Properties			
Physicals		Chemicals	
Solution fertilizer	Suspension fertilizer	Solution fertilizer	Suspension fertilizer
No crystal Pressure	Needle crystal No pressure	SG. 1.1-1.25 Low concentration $N+P_2O_5+K_2O$ =20-25%	SG. 1.3-1.6 High concentration $N+P_2O_5+K_2O$ >30%
Stored at cool place, No caking or Crystal	Stored at cool place, Caking but reverse to initial form easily	Complete in Plant nutrients	Complete in Plant nutrients
Good dissolved No precipitates Corrosive, clogging Expensive freight	Good dissolved No precipitates No Low freight		

Source: modified from Osotsapar (1993)

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Table 2 Comparison in physicals and chemicals properties between suspension fertilizer and conventional fertilizer

Properties	Type of fertilizer	
	Suspension	Conventional
Phase	Suspended liquid	Granular or powder
Plant nutrients	High analysis grade	High analysis grade
guarantee	$N+P_2O_5+K_2O$ = 20, >30%	$N+P_2O_5+K_2O$ = 20, >30%
Secondary-trace	Completely: Ca, Mg, S, Zn,	No or some
nutrients	Fe, Mn, Cu, B, Mo	
pH	6.5	3-5
Dissolve in water	Very good	Poor
Accurate and uniform	Yes	No
of nutrients		
Damage to roots	No	Yes
Rate of use	Less than (14-30% of conventional fertilizer)	More than
Compatible	Pesticides	No
Runoff and leaching	Less than	More than
Stored at normal temp.	Initial form	Caking, Melting
Protection to leaf burn	Yes	No
and diseases		
Change for fertilizer	Immediately	No
grade and rate of use		
Plant growth	continued	discontinued
Sample	21-7-14, 25-7-7, 8-24-24	21-7-14, 25-7-7, 8-24-24

Source: modified from Osotsapar (1993)

Fertigation system

Fertigation system consists of soluble fertilizer, pumping, injector, pipeline

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and emitter (**Figure 1**). It combines the application of irrigation water with fertilizers accurately and uniformly through the wetted area, where the active roots are concentrated at the same time. This remarkably increases the efficiency in the application of the fertilizer, which allows reducing the amount of applied fertilizer. This not only reduces the production costs but also lessens both the potential of groundwater pollution caused by the fertilizer leaching and runoff the fertilizer from root zones. This practice contributes to the achievement of higher yields and better quality. Other advantages of the fertigation are (Nantakij, 2002):

1. The saving of energy and labor.

2. The flexibility of the moment of the application (nutrients can be applied to the soil when crop or soil conditions would otherwise prohibit entry into the field with conventional equipment).

3. Convenient use of compound and ready-mix nutrient solutions containing also small concentrations of micronutrients which are otherwise very difficult to apply accurately to the soil.

4. The supply of nutrients can be more carefully regulated and monitored. When fertigation is applied through the drip irrigation system or micro-sprinkle, crop foliage can be kept dry thus avoiding leaf burn and delaying the development of plant pathogens.

5. To adapt the amount and concentration of the applied nutrients in order to meet the actual nutritional requirement of the crop throughout the growing season. To capitalize on fertigation benefits, particular care should be taken in selecting fertilizers and injection equipment as well in the management and maintenance of the system.

6. Use as a carrier for micronutrients, as liquids easily provide a homoge-

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neous mixture. For lime, when added to fluids in the form of a fine powder which would produce dust if applied dry, lime can be applied to the soil. The small lime particles added with fluids can rapidly increase soil pH.

7. Suspension fertilizer rate of application for fruit crops is less than 30% of broadcasting rate of application (Pichai, 2012; Kusakabe *et al.,* 2006; Thompson *et al.,* 2003).

8. Highly uniform and accurate distribution of water and fertilizers.

9. Minimized fertilizer loss due to localized application (to reduce leaching and runoff) (Montree, 1995).

10. Ability to change fertilizers for maximum yield.

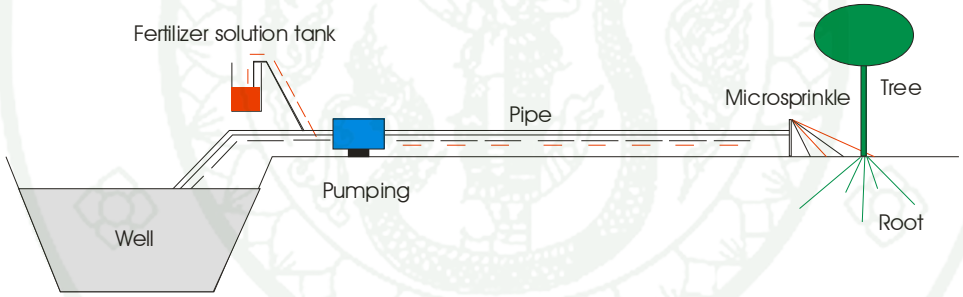

Figure 1 Fertigation system: well, pumping, pipe, microsprinkle and fertilizer solution tank

Suspension fertilizer production

History of liquid or fluid fertilizers (Achorn and Hargett, 1980)

In the terminology of the fertilizer industry, liquid or fluid fertilizers include clear solutions and clay suspensions. Clear solutions are produced by dissolving soluble fertilizer materials in water, and have a clear appearance. They are able to

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hold substantial amounts of nitrogen and phosphate in solution but have a limited ability to hold potash and micronutrients and are unable to hold lime. Clay suspensions are produced by adding clay such as attapulgite to a solution. The clay increases the viscosity and allows formation of a gel-like product which flows readily but will allow small solid particles to remain suspended for 24 to 48 hours with no agitation, or indefinitely with minor agitation. The use of suspensions allows desirable levels of potash, micronutrients and lime to be applied.

Fluids can also be classified as non-pressure or pressure fluids. Non-pressure fluids such as UAN or ammonium polyphosphate can be safely stored or applied using equipment at atmospheric pressure. Anhydrous ammonia, used in the US as a direct application fertilizer, is classed as a pressure fluid. It must be maintained under pressure to remain in the liquid form and changes to a gas at atmospheric pressure. The use of anhydrous ammonia requires highly specialized equipment and procedures.

Experiments with solutions of soluble mineral salts as fertilizers were carried out in the early 1800's. One of the first successful commercial operations was an early liquid fertilizer plant built in California in 1923, which was based on soluble fertilizer salts dissolved in water.

In the 1930's, **Hydroponics:** experiments were carried out with hydroponics, growing plants in dilute fertilizer solutions. These did not result in economically viable operations, but advanced knowledge of the use of fluids. Testing was also done with solutions containing ammonia, urea and ammonium carbonate.

In California in 1940, **Irrigation:** liquids were used in irrigation for the first time, when phosphoric acid produced by the furnace method was added directly to irrigation water in the western US.

In 1953, **Potassium Containing Fluids**: the first solution containing a fairly high level of potassium was produced in the US. Phosphoric acid was mixed with

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ammonia for the first time, and potash was added to the resulting hot solution, producing 4-10-10. Shortly afterwards, formulations such as 9-9-9, and 12-6-6 were produced, using urea. Application equipment at this time was in the early stage of development and was poorly designed.

Fluid fertilizers had now been shown to be a feasible method of providing plant nutrition, but farmers were not impressed. Fluids cost more per unit of nutrient than solid fertilizers. Farmers scoffed at the product, saying they were not interested in buying water. They demanded more concentrated products. An early liquid fertilizer, 8-24-0 sold for the same price per ton as its solid counterpart 16-48-0. The application equipment was poorly designed, corrosion caused problems, and lines and nozzles became plugged by salts precipitating out of the solutions.

Superphosphoric acid (SPA) Development: Conversion of phosphate rock into phosphoric acid produces an acid with a P_2O_5 content of around 30%. This product is evaporated to produce 54% P_2O_5 acid, also called “merchant grade”, in which the phosphate is in the orthosphosphate form (not polymerized). Evaporation to higher P_2O_5 levels removes water from the phosphate, causing it to polymerize to form polyphosphate. The product known as superphosphoric acid is generally concentrated to approximately 68-70% P_2O_5, where it contains 20-35% polyphosphate. Superphosphoric acid was first produced in 1956. In 1957 it was reacted with ammonia to produce a solution of approximately 11-33-0, and by 1960-62, 10-34-0 and 11-37-0. These polyphosphate solutions had very desirable properties. They formed stable complexes with metal ions such as calcium and magnesium that had formed undesirable precipitates that plugged equipment in the earlier solutions. The polyphosphate solutions also resisted salting out when cooled. These new developments minimized problems with plugged equipment.

Farmers now had access to high analysis liquid fertilizers which could effectively compete with solid fertilizers in cost per unit of nutrient. Further developments included adding lime, pesticides and micronutrients to suspensions, allowing farmers to make only one pass and providing crops with a better chance of

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fully using the fertilizer. The popularity of suspension fertilizers grew rapidly, and they were first used for aerial spraying in 1966.

Suspension fertilizer production method

Preferably, most of suspension fertilizer plants use liquid raw materials which are sources of Nitrogen: anhydrous NH_3, aqueous NH_3, sources of Phosphorous: ortho phosphoric acid (wet process 55% P_2O_5), super phosphoric acid (wet process 75% P_2O_5), solid ammonium phosphate (MAP), source of Potash: KCl (60% K_2O) and sources of suspending agents: clay, bentonite and gum, for suspension fertilizer production method. Thereby, the starters which are both the NP base suspension fertilizers and UAN are obtained such as 8-24-0, 10-30-0, 10-34-0, 12-40-0, 28-0-0, and 34-0-0 (Achorn and Hargett, 1980).

The methods are:

1. Usually to produce UAN solutions which are made from reaction between urea and ammonium nitrate. There are analysis grades of 28-0-0, 30-0-0, and 32-0-0.

2. To produce NP base solutions which are made from reaction among anhydrous NH_3, aqueous NH_3 and phosphoric acids. There are analysis grades of 8-24-0, 10-34-0 and 11-37-0.

3. Adding suspending agents

4. Adding source of potassium

5. Milling the pre mixed solution for the final product: suspension fertilizer.

In general, the first step to the fourth step is processed in tank reactor, pipe reactor, immersing tank and mixing tank respectively.

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Plant processing equipment

Fluid fertilizer manufacturing plants can range from a simple plant where anhydrous ammonia is mixed with water in a simple pipe system to produce aqua ammonia to a complex plant capable of producing several grades of both liquid and suspension fertilizers.

The list of plant processing equipment includes mixing tanks, mixers, pumps, pipes, valves, raw materials, storage bins and tanks, product storage tanks, flow meters, ammonia sparger, pre-weighing bins and tanks, coolers, silos, side mixing facilities and other optional components.

Mixing tanks

A vertical mixing tank which is open at the top and discharge at the side of bottom can contains depending on a desired capacity of liquid raw materials such as 10-25 tons. It can be made of mild steel, coated mild steel, or stainless steel. There are fittings to withdraw products at the base of the tank and the other fitting for recirculation the products. The inside of the tank may have baffles, cone bottoms and sparger, rotating stirring devices: simple paddles to turbine types to accentuate the products. This type of tank can be produced liquid fertilizers and suspension fertilizers.

Types of fluid manufacturing plants (Wolf *et. al.*, 1985)

1. Cold mixed plants
2. Hot mixed plants
3. Dry –fluidizing units
4. Pipe-reactor plants
5. Spray-reactor plants
6. The aqua ammonia converter

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1. Cold mixed plants

Cold mixed plants are relatively simple, and there are few major variations in their design. Storage tanks, meters, scales, and simple mix tank make up the equipments list. A typical cold mixed plant for production of either liquids or suspensions is shown in **Figure 2**. In these plants the base phosphate solutions, non-pressure nitrogen solutions and potash are weighed and mixed in the mixed tank; and the resulting solution or suspension is pumped to the product storage tank or applicator.

Another type of cold mixed plant is the satellite plant, shown in **Figure 3**, used by many companies. Base materials such as 10-30-0, 13-38-0 or 11-33-0 suspensions or 10-34-0 and 11-37-0 solutions are shipped along with NPK base solutions or suspensions and nitrogen solutions to the satellite plant. The base materials are mixed and weighed in a small mixed tank mounted on scales. With these base materials, an operator can install an inexpensive plant for the production of NPK suspensions and solutions near the point of distribution.

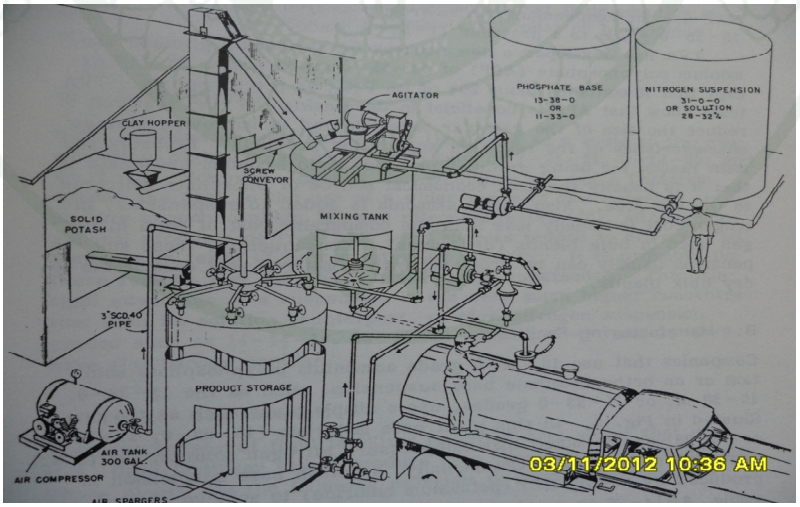

Figure 2 Cold mixed plant for production of suspension fertilizers
Source: TVA, Fluid Fertilizer Foundation (1972)

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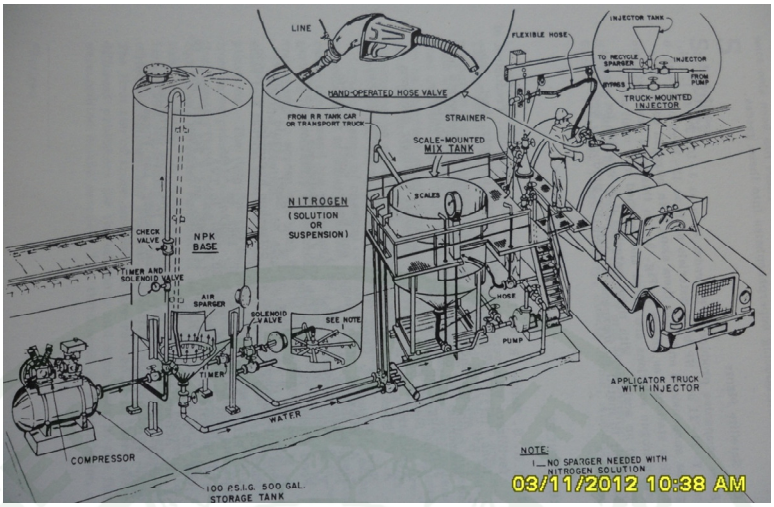

Figure 3 Suspension satellite plant

Source: TVA, Fluid Fertilizer Foundation (1972)

2. Hot mixed plants

One typical hot mixed plant is the TVA three-stage continuous ammoniation plant (Jones and Getsinger, 1979) for producing 13-38-0 orthophosphate base solutions, shown in **Figure 4**.

The acid is ammoniated in three stages, with precise temperature and pH control in each stage. In the first stage, the boiling reactor is operated at pH 5.4 to precipitate magnesium, iron and aluminum impurities in forms that will not produce gels during storage of the suspension. The second stage ammoniator is operated at 200°F and pH 6.5. Fluid from the second stage is rapidly cooled in an evaporative cooler. The rapidly cooling results in the formation of small crystals in the suspension. In the third stage, gelling clay and a small quantity of ammonia are added. The resulting 13-38-0 grade product is further cooled with a cooling coil. Various designs for hot mixed plants and direction can be obtained from TVA.

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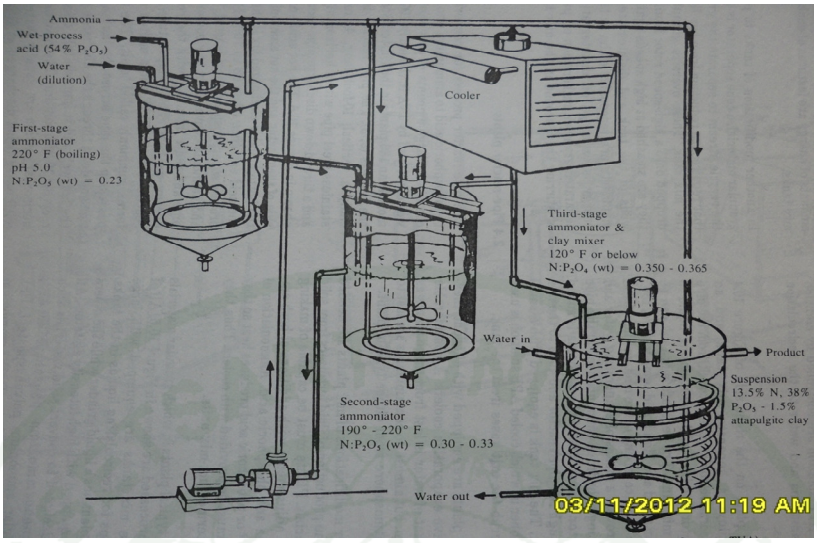

Figure 4 Three-stage continuous ammoniation process for production of 13-38-0 orthophosphate suspension

Source: Jones and Getsinger (1979)

Continuous hot mixed plants are normally used to make 10-34-0 and 11-37-0 ammonium polyphosphate (APP) base liquids using the pipe-reactor process. Two typical plants for the production of APP base liquids are shown in **Figure 5, 6.** The plant shown in **Figure 5** has a combination mix tank-cooler design. The upper part of the tank is filled with plastic "Pall Ring" packing. The liquid is partially cooled by recirculating it through this section while air is drawn through the section. Liquid from the bottom of the tank is passed through a heat exchanger where it is further cooled before it is pumped to storage. Anhydrous ammonia is passed through this same heat exchanger, vaporized and then passed into the tee section of the pipe reactor. Super phosphoric acid is pumped by a positive displacement pump to the tee section, where the acid and gaseous ammonia react to form a hot (600°F) melt. Water content and pH of the APP solution are controlled by addition of ammonia and water to the recirculation lines.

The plant in Figure 6 employs a separate mix tank and an evaporative cooler. The hot melt from the pipe reactor is mixed with recirculating liquid in the mix tank.

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The separate mix tank can be maintained at a high liquid temperature, 180°F, to enhance mixing of the melt and liquid and to provide a means of evaporating water and heating anhydrous ammonia used in the pipe reactor. About 60% of the ammonia is added through the pipe reactor and 40% to the mix tank. The mix tank is equipped with a small scrubber in which cooled APP solution is used to scrub the exit gases from the tank.

Both plants are equipped with efficient, inexpensive evaporative coolers. A considerable amount of water is lost from these plants as steam, but almost no contaminants are lost to the atmosphere from either type of plant.

Other modifications of mix plants are needed for the production of fluid fertilizers from solid materials. Plants must be capable of making ratio adjustments with addition of both ammonia and phosphoric acid. Ammoniation of MAP or phosphoric acid produces heat so they also must be provided with coolers. Thus, they are termed hot-mix units.

Five types plants in which granular materials are processed are shown in **Figure 7.** All of these mix tanks are equipped with large pumps for recirculating liquids in the tanks. One plant has a liquid grinder while the others are equipped with high-intensity agitators. All are designed to convert solid materials such as monoammonium phosphate (MAP), granular ammonium polyphosphate (APP), diammonium phosphate (DAP), ammonium sulfate, urea and potash to fluids.

All of these mixing tanks are equipped for adding ammonia, some for adding phosphoric acid (Achorn and Hargett, 1980). They can be used to convert solid materials (MAP, granular APP, DAP, ammonium sulfate and urea) to fluids. With this mixing equipment it is usually possible to produce about two batches or more per hour of an 11-33-0 grade base suspension from MAP or APP and ammonia. It is also used to produce high analysis suspension mixtures such as the 7-21-21, 3-10-30 and 14-14-14 grades.

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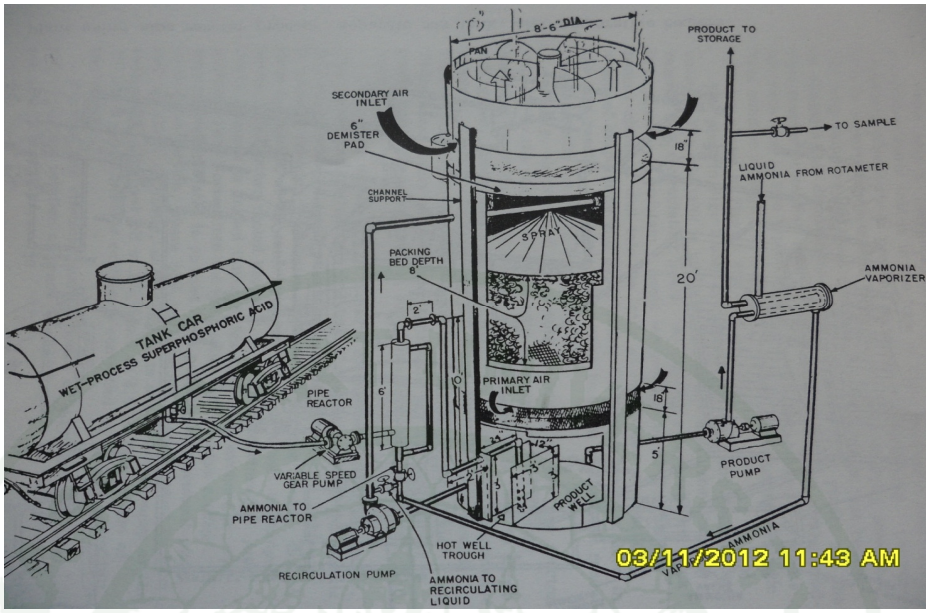

Figure 5 Plant using pipe reactor process with integral mix tank, cooler and scrubber

Source: Jones and Getsinger (1979)

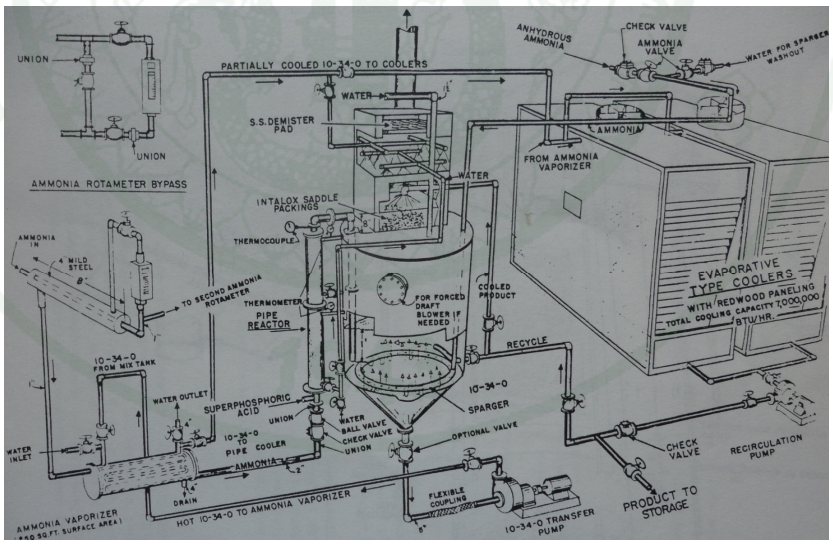

Figure 6 Plant using pipe reactor process, separate mix tank and evaporative cooler

Source: Jones and Getsinger (1979)

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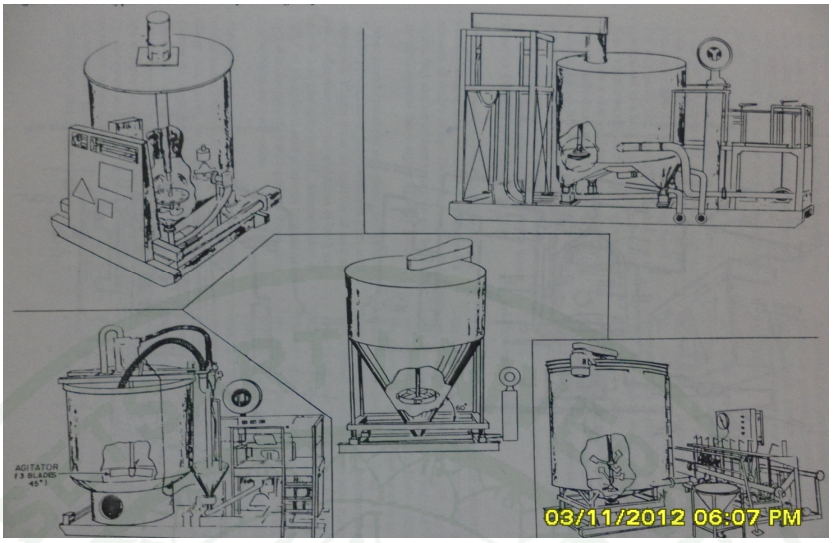

Figure 7 Five types of mix tanks for producing suspensions
Source: TVA, Fluid Fertilizer Foundation (1972)

3. Dry –fluidizing units

As pointed out previously in discussions of plants to process granular materials into fluids, large pumps that consume large amounts of energy are features of each of the mix tanks.

In another modification of tanks to process granular material, a cone separator is used in the recycle stream to separate the granules that require size reduction from the fluids in the mix tank. These oversize granules are dropped onto a high-speed rotor from which they are smashed at the high speeds against the walls of the tank and disintegrated. The manufacturer's reasonable claim is that the energy is expended on disintegrating the separated granules, rather than on pumping or stirring them around in the mix tank.

4. Pipe-reactor plants

Pipe-reactor process for converting orthophosphoric acid to ammonium

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phosphate containing large amounts of polyphosphates was developed by TVA in the early 1970's, and more than 130 plants in the United States use the process (Meline *et al*., 1972; Meline, 1973). The pipe reactor is essentially a vertical, 10-feet long, 4- or 6- inch stainless steel pipe with a horizontal section and a turned-down discharge pipe mounted as shown in **Figure 8.** The acid enters the side of the reactor, and the hot ammonia enters the bottom and is discharged six inches above the acid entrance when 68 to 70% P_2O_5 wet-process superphosphoric acid is used. The acid and ammonia converge in the bottom of the pipe and react instantly with the release of energy as heat. The temperature quickly reaches 600-650°F, and a molten material forms, commonly called "melt." The hot melt passed up the pipe across the horizontal section and down through the discharge pipe into the hot well and is immediately dissolved in recycled 10-34-0 solution. The reactor and the horizontal section are usually water-cooled, with water being discharged at 200°F. The product contains 40 to 60% polyphosphates.

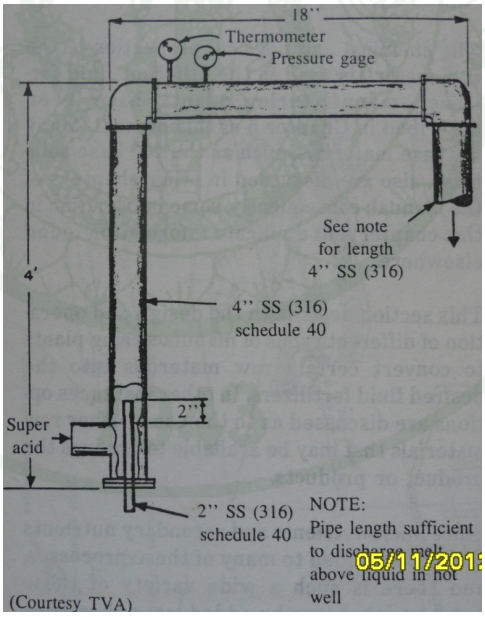

Figure 8 Diagram of plant-size pipe reactor

Source: TVA, Fluid Fertilizer Foundation (1972)

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There have been many modifications and designs of pipe reactors. The reactor used by TVA in its 20-ton-per-hour demonstration plant forproducing 9-32-0 suspension from 54% P_2O_5 wet-process phosphoric acid is shown in **Figure 9.** This reactor is 14 inches in diameter and 9 ft long. It features the acid-ammonia mixing tee as shown in **Figure 9**. Hot ammonia is fed through a 2-inch-diameter, lance type sparger that extends through the center of the tee and about 3 inches into the reactor. Hot acid enters the branch of the tee and flows through the annular space between the pipe tee and the ammonia sparger and into the pipe reactor. With this configuration, the 54% P_2O_5 wet-process phosphoric acid reacts with the hot ammonia to produce a melt temperature of about 450°F at the discharge end of the reactor. The APP melt contains 20 to 30% of its P_2O_5 as polyphosphate.

Portable pipe reactor plants have been designed and mounted on a large trailer. The sketch in **Figure 10** is a TVA design for such unit. The plant has a rectangular packed bed cooler that contain about 430 ft^3 of plastic 3-inch-diameter Pall rings. About 30,000 ft^3 of air per minute is pulled through the packing with a 6-ft-diameter fan. The basin has a capacity of about 700 gals of liquid depth of about 2 ft above the pump suction pipe. With a flat bottom, the capacity of the basin should be at least 1000 gals.

5. Spray-reactor plants

Other types of reactors have been patented for producing ammonium polyphosphate solutions, and at least one, the spray reactor (Harbolt and Young, 1977), is being used commercially in the United States. In the spray reactor a highly dispersed, unconfined acid spray is reacted with anhydrous ammonia vapor to form ammonium polyphosphate that fall into and dissolve in a pool of ammonium polyphosphate solution. Principle claim for the process are high conversion to polymeric species while minimizing both reactor fouling when using wet-process phosphoric acid, and corrosion when using electric furnace or “white” acids.

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6. The aqua ammonia converter

The aqua ammonia is usually produced near distribution centers from anhydrous liquid ammonia. A typical continuous plant is shown in **Figure 11**. Anhydrous is mixed with water and recycled with cooled aqua ammonia in a simple pipe mixing chamber. This type of plant can convert a 50-ton tank car of anhydrous ammonia into about 200 tons of aqua ammonia in five to eight hours. The rate of conversion depends on the size of cooling system for the plant. Water is added to adjust the specific gravity of the liquid to that of aqua ammonia containing 20.6% nitrogen (25% NH_3).

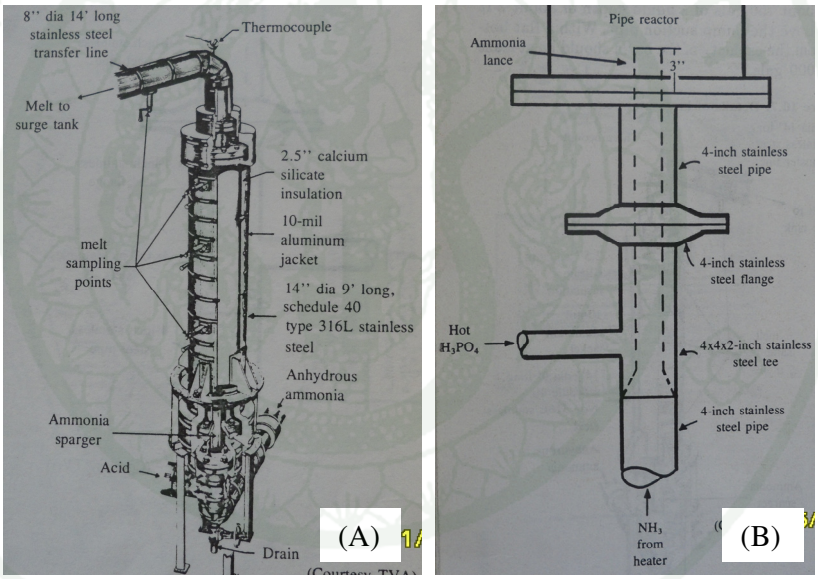

Figure 9 comparative pipe reactor, Details of large pipe reactor (A), Diagram of phosphoric acid-ammonia mixing tee (B)

Source: TVA, Fluid Fertilizer Foundation (1972)

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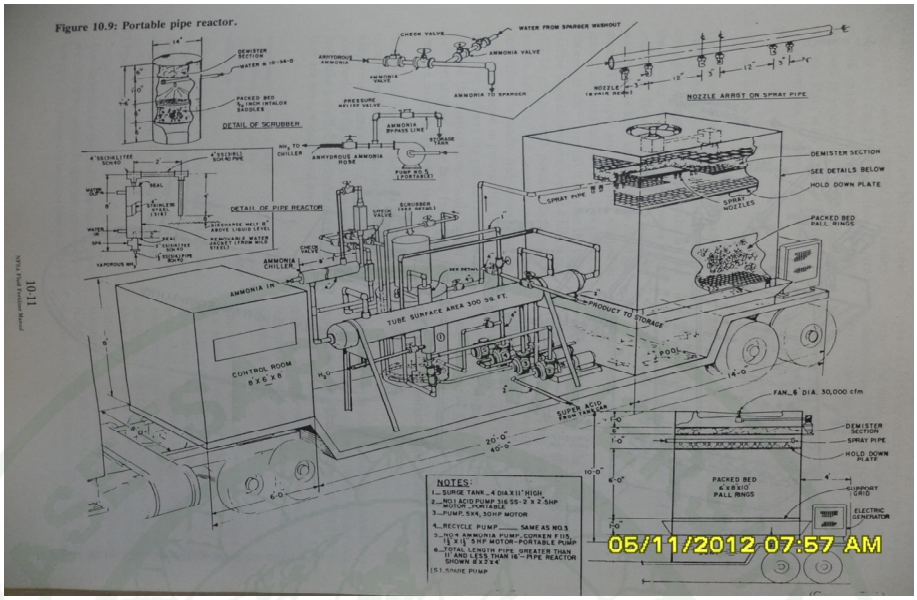

Figure 10 Portable pipe reactor

Source: TVA, Fluid Fertilizer Foundation (1972)

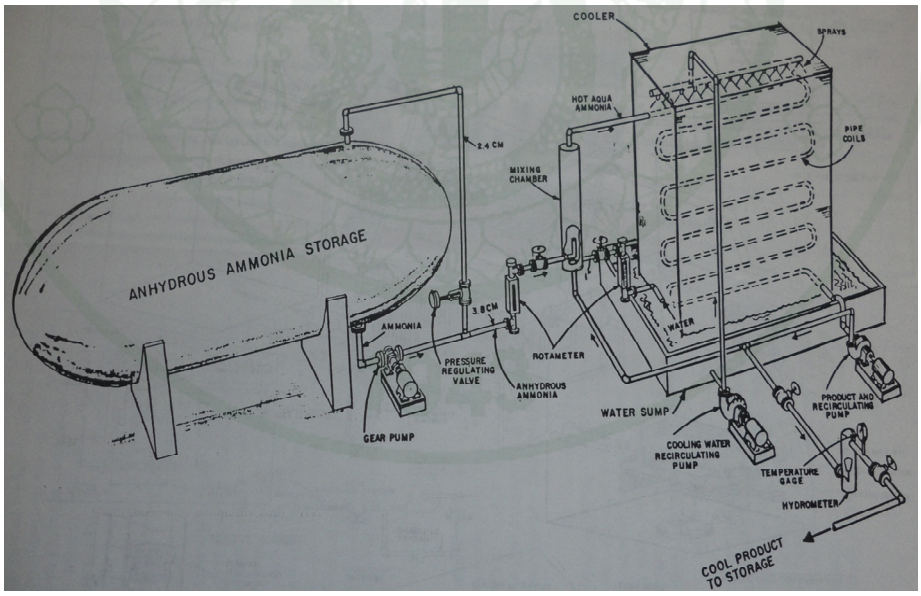

Figure 11 Continuous-type ammonia convertor

Source: TVA, Fluid Fertilizer Foundation (1972)

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The conventional methods of suspension fertilizer production are complicate as following:

1. To store anhydrous NH_3, aqueous NH_3 and Ortho phosphoric acid into the stored tanks through the pipes from a trailer truck. They can be found a leak out.

2. As processing, the liquid raw materials which are anhydrous NH_3, aqueous NH_3 and Ortho phosphoric acid can leak out from connecting pipes and processing tanks.

3. There are more temperature and more pressure which are obtained from the reaction among them. Entire steps are unsafely and chance of explosion.

The conventional processes for the suspension fertilizer production are following (TVA, Fluid Fertilizer Foundation, 1972):

1. To be stored the liquid raw materials in the stored tanks by transferring from tank trucks to them through the pipes.

2. Usually to produce UAN solutions which are made from the reaction between urea and ammonium nitrate. They are analysis grades of 28-0-0, 30-0-0, and 32-0-0 (Salladay and Kachelman, 1986)

3. To produce NP base solutions which are made from the reaction among anhydrous NH_3, aqueous NH_3 and phosphoric acid. They are analysis grades of 8-24-0, 10-34-0 and 11-37-0 (Leikam, 2008).

4. Adding suspending agents: actually use clay

5. To produce the complex suspension fertilizers: 15-15-15, 15-5-20, 25-7-7 and etc. by adding source of potassium

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6. Milling the pre mixed solutions for the final products: the complex suspension fertilizers. In general, the second steps to the fifth steps are processed in tank reactor, pipe reactor, immersing tank, cooling tower and mixing tank respectively (**Figure 12**).

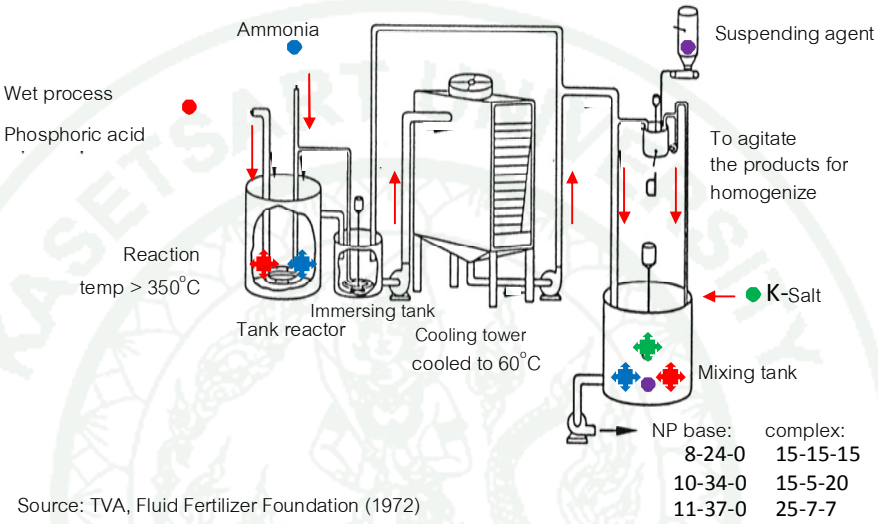

Figure 12 The scheme of suspension fertilizer production method
Source: TVA, Fluid Fertilizer Foundation (1972)

The interesting points in the conventional process

From the schemes that were said before, there were many interesting points that would be researched and developed as following.

1. **High investment cost:**

On **Figure 13,** a 1998 UNIDO/IFDC estimate of the cost of installing a fluid fertilizer plant was US $200,000 to $400,000, depending on the desired equipment. Equipment in a pipe reactor plant must be capable of withstanding the high pressures, temperatures and corrosion that are a part of producing ammonium polyphosphate. A liquid mix plant has relatively simple equipment that blends

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together materials produced elsewhere. A cold mix plant for suspensions has capability for adding clay to build viscosity, and must have mixers, pumps and piping capable of handling higher viscosity materials. A batch plant requires pressurized equipment for holding ammonia. A suspension satellite plant is a smaller plant that obtains small batches of pre-mixed suspension or liquid fertilizer product from other plants, does some mixing, and dispenses the suspension product.

Equipment Cost Table

Equipment and Installation (20 tph capacity)	Investment Cost (US $)
Pipe reactor plant for ammonium polyphosphate	400,000 (limited storage)
Liquid fertilizer mix plant	275,000
Cold mix plant for suspensions	400,000
Batch plant using liquid ammonia and phosphoric acid	400,000
Suspension satellite plant	200,000

Figure 13 Equipments, installation and equipment cost
Source: UNIDO/IFDC (1998)

1. **High temperature and high pressure:**

When the ortho phosphoric acids are being fed into a tank reactor by a connecting pipe, immediately, anhydrous NH_3 and potassium are being fed into them by the other connecting pipes also. The reaction would be occurred with high temperature which is more than 750 ^{0}C. Certainly there is a high pressure. Thereby, it risks of explosion.

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1. **Complicatedly to handle liquid raw materials:**

Anhydrous NH_3 and aqueous NH_3 which are alkaline substances can volatilize easily to NH_3 gas and can leak out from the pipes or stored tanks. Ortho phosphoric acid is a strong acid, which can leak out also.

2. **Complicatedly to produce the UAN solutions:**

Actually, UAN is received by reaction between urea and ammonium nitrate. For Thailand, ammonium nitrate is complicatedly imported because it is an explosive material which would be very difficultly allowed in by The Ministry of Defense.

3. **Many tanks and cooling tower:**

The previous suspension fertilizer production methods are consisted of long process and many tanks which are tank reactor, immersing tank, cooling tower, stored tank and transportation. It is difficult to managements.

4. **High maintenance and corrosive**:

According to many tanks and pipes, it would be more strictly maintenances which involve whole parts of equipments such as tanks, pipes, joints, valves, and pumps. It would be protected to corrosive, leak out, high temperature, high pressure and explosion.

All of the interesting points mentioned above affect on complicatedly process and many limitations for suspension fertilizer production.

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Factors affecting the stability of suspension fertilizers

1. Polyphosphate Content: a good ammoniation reaction of orthophosphoric acid is an N: P_2O_5 ratio which is 0.294 to 0.297 (Leikam, 2008).

2. Solution pH and metal ions

Hot mix plant, one of the suspension fertilizer production plants is the TVA three-stage continuous ammoniation. The acid is ammoniated in three stages, with precise temperature and pH control in each stage. In the first stage, the boiling reactor is operated at pH 5.4 to precipitated magnesium, iron and aluminum impurities in forms that will not produce gels during storage of the suspension. The second stage ammoniation is operated at 200°F and pH 6.5. Fluid from the second stage is rapidly cooled in an evaporative cooler. These rapid cooling results in the formation of small crystals are in the suspension. In the third stage, gelling clay and a small quantity of ammonia are added for pH 7.1 for converting any mono-ammonium phosphate to di-ammonium phosphate which crystallizes as very small crystals that are much easier to suspend. At last, the finished products are obtained (Jones and Getsinger, 1979). Moreover, the more than pH 5.9 in solution gave more crystals of DAP and less than pH 5.9 gave more MAP which could grow up in large crystals (Kendrick, Jr, 1974), the proper pH of the appropriated suspension fertilizers varied from 7.5 to 8 (Miller, 1962).

3. Temperature and time

Processing temperature: rapidly cooled to normal temperature results in the formation of small crystals in the suspension (Jones and Getsinger, 1979). Slack and Walters (1963) who found that the temperature 60°C to 96°C of solution effected on 3.3% of retained large crystal on 20 mesh test sieve which effected on a clogged nozzle. As the temperature was rapidly reduced to temperature 29°C, the crystals were small. Furthermore, Fox and Oldland (1976) who found that the formulated suspensions with temperature 38°C and pH 6 to 6.5 were for good stored period and

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loaded for shipment while the single stage procedure for suspension fertilizers was agreed with the temperature 70°C to 82°C (Kendrick, Jr., 1974).

Stored temperature: being stored at higher temperature effects on large crystals of soluble nutrient materials which are in suspended phase passes to dissolved phase while the fertilizer is subsequently cooled large crystal precipitate (Eibner *et. al*., 1985). Moreover, the large crystals in the suspension fertilizers would grow up after the products were stored for more times (Trimbach and Villard, 1970).

4. Suspending agent

Actually, suspension fertilizers consist of two phase's system where the continuous phase is saturated solution and where the discontinuous phase is a solid or liquid that is insoluble in the continuous phase. To stabilize such system, a suspending agent to gel the continuous phase is required. The continuous phase may contain nonionic materials: urea, thiourea and polyglycol surfactants, the cations: Na^+, K^+, NH_4^+, Fe^{3+}, Al^{3+}, Ca^{2+} and Mg^{2+}, the anions: Cl^-, SO_4^{2-}, PO_4^{3-}, NO_3^- and condensed phosphate and insoluble compounds with colloidal dimension. Since the continuous phase contain $mono^-$ and polyvalent anions and cations at ionic concentration, a gelling agent must be used that can be re-flocculated to form a stable gel structure in such an environment. The gelling agent is usually a clay mineral whose particles have to be dispersed and its crystal agglomerates broken up to increase the gelling power. When they are incorporated into a mixture, they flocculate or re-flocculate to impart the gel structure (Sawyer, 1982; Nichols and Elrod, 1988; Hemzacek and Sawyer, 1987). A suspension with sufficient gel strength will support the solids contained in the suspension and prevent them from setting out (Johnson and Huber, 1991).

5. Particle size

It can be provided for two types:

5.1 Particle size of raw materials: being 100 to 1000 micron (18 to 140

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mesh) (Aijala and Ahlnas, 1998).

5.2 Particle size of final product:

5.2.1 Particle size of crystal of raw materials being dissolved in the first stage (continuous phase): needle crystal of urea

5.2.2 Particle size of non-dissolved raw materials being suspended in the second stage (discontinuous phase): 90% of the solids with particle size in 0.1-1 mm, the remaining 10% with less than 0.1 mm (Trimbach and Villard, 1970), 92.5% of minus 20 mesh was properly for application by spraying through a 0.072 inch nozzle (Slack and Walters, 1963), being less than 50 micron (Aijala and Ahlnas, 1998), solid particles in the final suspension should not be coarser than 20 mesh (0.03 inch or 0.8 mil in diameter) and preferably should be finer (Wolf *et. al*., 1985), the average particle size should be about 4 µm with a maximum of 5% over 10 µm for active materials of density lower than 1.5. For active ingredients of higher density, it is preferable to go down to 3 µm with a maximum of 5% between 5 and 8 µm. It is also important to bear in mind that for certain active ingredients, an excessive fineness (< 1.5 µm) can greatly increase phytotoxicity and crystal growth. For some active ingredients this fineness can improve the biological efficacy. This must be checked in any case. (Leikam, 2008)

6. Speed of agitator and mixing time

The tip speeds of agitator for agitating the raw materials in suspension fertilizers are varied from 430 to 4300 rpm (Salladay and Kachelman, 1986; Boles, 1988) and the suitable speed for formulating suspension fertilizers is at least 9000 rpm (Mackinnon, 1978). The mixing time for the suspension is varied from 5 to 30 minutes (Salladay and Kachelman, 1986).

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The properties of appropriate suspension fertilizers

The following properties are required: long term storage stability (no settlement, low rate of crystal growth, stable rheological behavior etc), fairly low viscosity (easily pourable, facilitation handling, periodical stirring during storage and readily dispersible in water), good stability of the diluted dispersion at the application rate of use, no pressure (Leikam, 2008; Frangioni *et. al.*, 1976)

The benefits of the appropriate suspension fertilizers are as follows:

Good efficiency due to the smaller particle size, high concentration in $N+P_2O_5+K_2O$, complete in plant nutrients, compatibility to pesticides, prevention to disorder of some secondary and trace elements: Ca, Mg, Fe, and Zn, less rate of use, low packaging volume, non corrosive to equipments, non pressure (Leikam, 2008).

The rheological parameters for appropriate suspension fertilizers

Chemical property

The suspension fertilizers are evaluated in chemical property by analyze for N, P_2O_5 and K_2O (AOAC International, 2000)

Physical properties:

The suspension fertilizers are evaluated in physical properties as follows:

pH

Measurements of pH are especially important in the production of solutions and suspensions that involve ammoniation of phosphoric acids with ammonia. During production, pH measurements are used to monitor the ammonia to phosphoric acid ratio, and the pH of final product is adjusted to obtain the optimum solubility of the

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fluid being produced. pH meter with standardization control, temperature compensation, function switch and electrode holder is equipment for measurement (Wolf *et. al*., 1985).

Specific gravity

Specific gravity is defined as the weight of a substance compared to the weight of an equal volume of water at specified temperatures (Palgrave, 1991). Specific gravity measurements tell many things about the relative compositions of fluid fertilizers when correlated with other data for the particular solution or suspension. They are commonly made at 25°C and are useful in adjusting the calibrated application equipment to obtain accurate application rates for the particular fluid fertilizers. Hydrometer is equipment for measurement (Wolf *et. al*., 1985).

Stability

Stability of suspension fertilizers is determined to demonstrate that a sufficient amount of active substance is suspended in the initial liquid to give a satisfactory, homogeneous mixture during stored periods (APVMA, 2005) The measurement is by filling a known volume with the suspension to a graduated cylinder and allowing the cylinder to stand undisturbed for 24 hours. At the end of this time, the volume of clear liquid on the top of the suspension is determined and subtracted from the total volume of the suspension to give the volume of suspended solids. The volume of suspended solids is divided by the total volume multiplied by 100 gives the percent apparent solids which are shown in **Table 3** with stability (Browder and Ulmer, 1971). Actually, the formation of a clear liquid layer on top of a fertilizer suspension is cause by a contraction of the clay due to insufficient gel strength (Johnson and Huber, 1991).

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Table 3 % apparent solids affected on stability of the suspension

% Apparent solids	Stability
100	excellent
95-99	very good
90-94	good
less than 90	un-satisfactory

Source: Browder and Ulmer (1971)

Pour-ability

Data are required to demonstrate that the user can make use of the maximum amount of the product in the container and that an excessive amount of the material does not remain in the container (APVMA, 2005). The measurement is the % of the remaining products that 100 grams of suspension fertilizers are added into a jar that allows standing for a given period time. For each period, the jar is tilted to a 45^0 angle for 30 seconds. The amount of poured suspension fertilizers are obtained to determine. The jar is rinsed to receive the amount of remaining suspension fertilizers which are determined. Acceptable limits: max 5% residue; max 0.25% rinsed residue (CIPAC, 2009a; Salladay and Kachelman, 1986).

Viscosity

The viscosity of a fluid is the property that determines the resistance offered to a shearing force under laminar flow conditions. This method is intended for characterizing the flow behavior of liquid (APVMA, 2005). Actually, Brookfield Viscometer Model RVT is used. It includes operating at 100 rpm, using spindle No. 3 to be obtained viscosity < 1000 cps and using spindle No. 4 to be obtained viscosity < 2000 cps. The finished suspension fertilizers are measured by Brookfield Viscometer for a given period time and temperature. Its viscosity depends on analysis grade of suspension fertilizers, 100-2000 cps in limits, 300-600 cps in preference and 400 cps in most preference at 26.7^oC (CIPAC, 2009c; Salladay and Kachelman, 1986;

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Davenport *et. al*., 1978), the ideal condition of maximum possible gel strength and minimum possible viscosity (Johnson and Huber, 1991).

Salting out

Salting out which is evaluated by wet sieve analysis determines the quantity of particles in a formulation collected on a screen after dilution in water. The residue remaining on a sieve is determined after dispersion to ensure that no unacceptable residue remains, which can cause blockage of nozzles in application equipment (APVMA, 2005). The measurement is determined by sieving 100 grams of the product through a standard screens (three inch diameter 20 mesh). They are followed by washing with a cold water/acetone mixture and then with straight acetone. Crystals retained on the screens are dried and weighed to determine weight percent. Acceptable limits: Maximum 2% retained on a 20 mesh sieve (CIPAC, 2009b; Byrd and Scott, 1979).

The ideal suspension fertilizer production

This research is aimed to use solid phase raw materials instead of liquid NH_3, phosphoric acid, UAN, and NP base solutions. They are mono potassium phosphate phosphate (MKP: 0-52-34), urea (46-0-0), and potassium chloride (KCl: 0-0-60).

The ideal methods (hypothesis) will be following:

1. To cut out the tank reactors, the immersing tank, the cooling tower, the stored tanks, and the pipes for feeding the liquid raw materials. A new mixing tank is established with installed agitator inner.

2. To divide totals of solid raw materials into 2 parts, the one for clear liquid mixed solution stage, the other for suspended solution stage.

3. The principle of these methods is as flowing

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- Solubility (Mier's theory)
- Van der Waals force and gravitational force
- Fluids
- Suspension property
- Rheology

4. No chemical reaction
5. The suitable suspending agents
6. The speeds of agitator
7. To increase the temperature of solution
8. Controlling pH in the processing
9. Milling the solid raw materials for the appropriate size with a disc mill
10. Milling the pre mixed solution for the expected size of finished product with a bead mill
11. The chemical and physical properties of the finished product
12. The production methods having not been investigated before

Urea-ammonium nitrate solution (UAN) (International Plant Nutrition Institute, 2012)

Urea-ammonium nitrate solution (UAN) fertilizer is popular in many agricultural areas because they are safe to handle, convenient to mix with other nutrients and chemicals, and are easily applied. Furthermore, they are used as raw materials in formulating liquid or suspension fertilizer plants. They are relatively simple to produce. A heated solution containing dissolved urea is mixed with a heated solution of ammonium nitrate to make a clear liquid fertilizer. Half of the total N comes from the urea solution and half from the ammonium nitrate solution. UAN is made in batches in some facilities or in a continual process in others. No emissions or waste products occur during mixing.

Since UAN is a concentrated N solution, its solubility increases as the temperature rises. To prevent the N components from precipitating as crystals, UAN

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UAN solutions are made more dilute in regions with cold winter temperatures. Therefore, the N concentration in commercial UAN fertilizers will vary from 28% N to 32% N depending on geography (**Table 4)**. A corrosion inhibitor is usually added to the final solution to protect the steel in storage tanks (International Plant Nutrition Institute, 2012)

Table 4 Compositions, grade and physical properties of UAN

Properties	Grade of UAN		
Composition (% by weight)	28% N	30% N	32% N
Ammonium nitrate	40	42	44
Urea	30	33	35
Water	30	25	20
Salting out temperature (^{o}C)	-18	-10	-2
Solution pH		approximately 7	

Source: International Plant Nutrition Institute (2012)

Ammonium polyphosphate (APP: NP base suspension fertilizers) (Leikam, 2008)

Ammonium polyphosphate solution (10-34-0 and 11-37-0) is the most common liquid P fertilizer material in the U. S. today. APP can commonly be found throughout the fertilizer industry as the NP base suspension fertilizers. Most of the APP produced today is made by the pipe reactor process. In this process, wet-process super phosphoric acid and anhydrous ammonia are reacted in a "pipe" to produce a melt that has a temperature of 600° F to 700° F and a polyphosphate content of 70% to 75%. After the initial reaction in the pipe, the melt must be rapidly cooled, diluted with water, and further neutralized with ammonia to maintain the high polyphosphate content and resultant high quality. At the time of manufacturing, the APP should have the following properties (**Table 5**):

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Table 5 Grades and physical properties of polyphosphoric acids

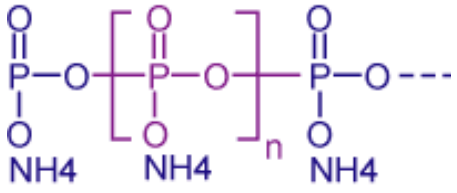
Characteristic	Grade of polyphosphoric acid	
	10-34-0	11-37-0
pH (depending on acid source)	5.8 to 6.2	5.8 to 6.2
Density (lb/gal)	11.65	11.90
% N by weight	10.0	11
% P_2O_5	34.0	37
N: P_2O_5 ratio	0.294	0.297
polyphosphate content (%)	65 to 75	65 to 75
salting out (^oF)	0	32

Source: Leikam (2008)

Ammonium polyphosphate (Specialchem, 2012) is an inorganic salt of polyphosphoric acid and ammonia. The chain length (n) of this polymeric compound is both variable and branched, and can be greater than 1000. Short and linear chain APPs (n < 100) are more water sensitive (hydrolysis) and less thermally stable than longer chain APPs (n >1000), which show a very low water solubility (< 0.1 g/ 100 ml). Liquid complex fertilizer process is represented by equation as follows:

$$NH_4OH + H_3PO_4 \longrightarrow NH_4PO_3 + 2H_2O$$

Chemical Formula and structure: $[NH_4\ PO_3]_n$ as below



APP Structure

APP is a stable, non-volatile compound. In contact with water APP it slowly gets hydrolyzed to mono ammonium phosphate (orthophosphate). Higher

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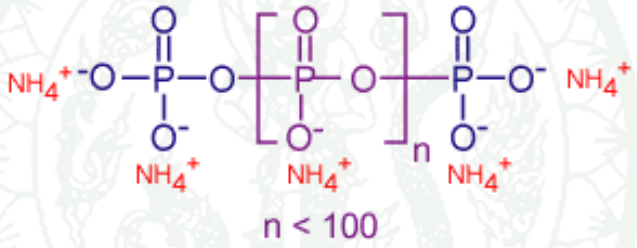
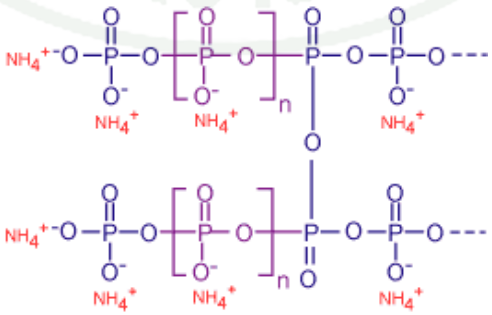
temperatures and prolonged exposure to water will accelerate the hydrolysis. Long chain APP starts to decompose at temperatures above 300 °C to poly phosphoric acid and ammonia. Short chain APP will begin to decompose at temperatures above 150 °C. There are two main families of ammonium polyphosphate: Crystal phase I APP (APP I) and Crystal phase II APP (APP II).

Crystal phase I APP (APP I) is characterized by a variable linear chain length, showing a lower decomposition temperature (aprox. 150°C) and a higher water solubility than Crystal Phase II Ammonium Polyphosphate. The general structure of APP is given below. In APP I, n (number of phosphate units) is generally lower than 100.



APPI Structure

Crystal phase II APP (APP II) as shown in below, APP II structure is cross linked / branched. The molecular weight is much higher than APP I with "n" value higher than 1000. APP II has a higher thermal stability (decomposition starts at approximately 300°C) and lower water solubility than APP I.



APPII Structure

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Properties of the possible solid raw materials

Urea (46-0-0) (Curtis J. *et.al*., 2012)

Urea Standards

Urea, white crystalline solid containing 46% nitrogen, is widely used in the agricultural industry as an animal feed additive and fertilizer. The UN's Food and Agriculture Association defines standards for fertilizers such as urea against which quality may be judged. For free-flowing urea, 90 percent or more of the granules should be able to pass through a 2.8 millimeter sieve yet not be able to pass through a 1 millimeter sieve, and no more than 5 percent overall should pass through the 1 millimeter sieve. In other words, the bulk of the granules should fall in the 1 to 2.8 millimeter range.

Physical Forms of urea

Commercially, fertilizer urea can be purchased as prills or as a granulated material. In the past, it was usually produced by dropping liquid urea from a "prilling tower" while drying the product. The prills formed a smaller and softer substance than other materials commonly used in fertilizer blends. Today, though, considerable urea is manufactured as granules. Granules are larger, harder, and more resistant to moisture. As a result, granulated urea has become a more suitable material for fertilizer blends.

Advantages of Fertilizer Urea

- Urea can be applied to soil as a solid or solution or to certain crops as a foliar spray.
- Urea usage involves little or no fire or explosion hazard.
- Urea's high analysis, 46% N, helps reduce handling, storage and transportation costs over other dry N forms.

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- Urea manufacture releases few pollutants to the environment.
- Urea, when properly applied, results in crop yield increases equal to other forms of nitrogen.

Blending urea with Other Fertilizers

Urea and fertilizers containing urea can be blended quite readily with monoammonium phosphate (11-52-0) or diammonium phosphate (18-46-0). Urea should not be blended with superphosphates unless applied shortly after mixing. Urea will react with superphosphates, releasing water molecules and resulting in a damp material which is difficult to store and apply.

Fluid urea

Uniformity of particle size is important with dry solid urea, whether applied directly or in blended formulations. Some imported urea appears to be below U.S. quality standards on granule uniformity. Dissolving urea and marketing the liquid solution is an attempt to overcome this lack of uniformity and still take advantage of the favorable urea price.

The liquid mix of urea and ammonium nitrate (UAN 28% N) has been on the market for a long time. The characteristics of this solution, however, are not the same as when urea alone is dissolved in water. A solution of 50% urea by weight results in 23-0-0 and has a salting-out temperature of 60 degrees F. In order to store and handle liquid urea during cooler temperatures, the nitrogen concentration must be lowered to reduce salting problems. There are several possible formulations that can be used for this, such as adding small amounts of ammonium nitrate, ammonium sulfate, or anhydrous ammonia.

Research, particularly on liquid urea, is very limited. Generally, where dry urea functions successfully, the fluid urea should perform equally well and may have the advantage of better uniformity over some dry urea sources.

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Biuret in Urea

Biuret in urea can cause agronomic problems if placed near the seeds or even if added preplant in bands where seeds will later be planted. Most U.S. manufacturers of urea keep biuret content low by keeping high temperatures to a minimum. Biuret content is typically around 0.3%, although urea of foreign origin appears to be higher.

High heat is normal during the manufacture of urea. If heat exceeds 200 degrees F there is a slight conversion of urea to biuret, but this takes place only during the manufacturing process. No such conversion happens in storage or in the soil.

Biuret converts to ammonia, but conversion is much slower than for urea. Since biuret remains in the soil for several weeks, the potential for seed damage continues beyond the brief period of conversion of urea to ammonia. The major damage of biuret is to germinating seeds. There is little damage through plant absorption, although some citrus crops have been affected.

Urea Storage

Urea is neither combustible nor explosive. It can be stored safely with no loss of quality under normal circumstances. Small or fast-moving augers should not be used to move granular urea. Urea particles are generally soft and abrasion can break the granules. Belt conveyers should be used whenever possible.

Urea should not be stored with ammonium nitrate. These materials, when in contact, rapidly absorb water when the relative humidity is above 18%. Table 9 indicates the relative humidity at which urea and ammonium nitrate absorb moisture from the air.

Production (International Plant Nutrition Institute, 2012)

The production of urea fertilizer involves controlled reaction of ammonia gas (NH_3) and carbon dioxide (CO_2) with elevated temperature and pressure. The molten

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urea is formed into spheres with specialized granulation equipment or hardened into a solid prill while falling from a tower.

During the production of urea, two urea molecules may inadvertently combine to form a compound termed biuret, which can be damaging when sprayed onto plant foliage. Most commercial urea fertilizer contains only low amounts of biuret due to carefully controlled conditions during manufacturing. However, special low-biuret urea is available for unique applications.

Urea manufacturing plants are located throughout the world, but most commonly located near NH_3 production facilities since NH_3 is the major input for urea. Urea is transported throughout the world by ocean vessel, barge, rail, and truck.

Chemical Properties

Chemical Formula: $CO(NH_2)2$

N content: 46% N

H_2O Solubility (20 ºC) 1,080 g/L; 167 g U/100 g water 40^oC (Osotsapar, 1993)

Solution pH (1% in water 25 ºC) 7.53

Specification granule Urea

1. Nitrogen : 46% by weight minimum.
2. Moisture : 0.5% by weight maximum.
3. Biuret : 1.0% by weight maximum.
4. Size : 90% Minimum between 2 mm and 4 mm
5. Physical condition: urea shall be essentially spherical and uniform in size, coated and shall have a hard smooth finish and shall be free flowing.

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Mono ammonium phosphate (MAP: 12-60-0)

(International Plant Nutrition Institute, 2012)

Mono ammonium phosphate (MAP) is a widely used source of P and N. It is made of two constituents common in the fertilizer industry and has the highest P content of any common solid fertilizer.

Chemical Properties

Chemical formula: $NH_4H_2PO_4$

P_2O_5 range: 48 to 61%

N range: 10 to 12%

Water solubility (20º) 370 g/L

Solution pH 4 to 4.5

Agricultural Use

MAP has been an important granular fertilizer for many years. It is water soluble and dissolves rapidly in soil if adequate moisture is present. Upon dissolution, the two basic components of the fertilizer separate again to release NH_4^+ and $H_2PO_4^-$. Both of these nutrients are important to sustain healthy plant growth. The pH of the solution surrounding the granule is moderately acidic, making MAP an especially desirable fertilizer in neutral and high pH soils. Agronomic studies show that there is no significant difference in P nutrition from various commercial P fertilizers under most conditions.

Granular MAP is applied in concentrated bands beneath the soil surface in proximity of growing roots or in surface bands. It is also commonly applied by spreading across the field and mixing into the surface soil with tillage. In powdered form, it is an important component of suspension fertilizers. When MAP is made with especially pure H_3PO_4, it readily dissolves into a clear solution that can be used as a

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foliar spray or added to irrigation water. The P_2O_5 equivalent content of high-purity MAP is usually 61%.

Management Practices

There are no special precautions associated with the use of MAP. The slight acidity associated with this fertilizer reduces the potential for NH_3 loss to the air. MAP can be placed in close proximity to germinating seeds without concern for NH_3 damage. When MAP is used as a foliar spray or added to irrigation water, it should not be mixed with calcium or magnesium fertilizers. MAP has good storage and handling properties. Some of the chemical impurities (such as iron and aluminum) naturally serve as a conditioner to prevent caking. Highly pure MAP may have a conditioner added or may require special handling to prevent clumping and caking. As with all P fertilizers, appropriate management practices should be used to minimize any nutrient loss to surface or drainage water.

A high purity source of MAP is used as a feed ingredient for animals. The NH_4^+ is synthesized into protein and the $H_2PO_4^-$ is used in a variety of metabolic functions in animals.

Non Agricultural Uses

MAP is used in dry chemical fire extinguishers commonly found in offices, schools, and homes. The extinguisher spray disperses finely powdered MAP, which coats the fuel and rapidly smothers the flame.

MAP Production (Manel *et al*., 2012)

Ammonium phosphates are produced by reactions (neutralization) between ammonia and phosphoric acid resulting in the formation of mono-basic, di-basic or tri-basic salts. When the mole ratio of nitrogen from ammonia and phosphorus from phosphoric acid is 1.0, mono-ammonium phosphate (MAP: $NH_4H_2PO_4$) is formed,

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and when the mole ratio is 2.0, di-ammonium phosphate [DAP: $(NH_4)_2HPO_4$] is formed. The reaction is exothermic, so the MAP and DAP are produced at an elevated and relatively constant temperature of 110℃. The equations for the neutralization reaction between ammonia and phosphoric acid are as follows:

$$NH_3(g) + H_3PO_4(aq) \rightarrow NH_4H_2PO_4(s)$$
$$NH_3(g) + NH_4H_2PO_4(aq) \rightarrow (NH_4)_2HPO_4(s)$$
$$NH_3(g) + (NH_4)_2HPO_4(aq) \rightarrow (NH_4)_3PO_4(s)$$

The mono-ammonium phosphate (MAP) tends to produce crystals of needle form while the di-ammonium phosphate (DAP) results in more granular forms of crystals. Tri-ammonium phosphate (TAP: $(NH_4)_3PO_4$) is an unstable crystal and less soluble than MAP and DAP. MAP and DAP are used as a main source of phosphorus in fertilizers. Several important characteristics of MAP, DAP and TAP are identified in **Table 6**.

Table 6 Properties of ammonium phosphates salts (MAP, DAP and TAP)

Properties	$NH_4H_2PO_4$ (MAP)	$(NH_4)_2HPO_4$ (DAP)	$(NH_4)_3PO_4$ (TAP)
Molar mass (g/mol)	115	132	149
Specific gravity at 20 ℃	1.803	1.619	N/A
Heat of formation (cal)	29.000	48.500	58.400
Solubility at 25 ℃ (g/100g water)	40	69.5	17.7
Ammonia vapor pressure at 100 ℃ and 125 ℃ (mmHg)	0.00 and 0.05	5.00 and 30.0	643 and 1177
pH of 0.1M solution	4.4	8.0	9.4
Crystal form	Tetragonal	Monoclinic	Orthorhombic

Source: Ross *et al*. (1929)

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Mono potassium phosphate (MKP: 0-52-34) (Wenkem, 2012)

MKP (KH_2PO_4) is a fully water-soluble P_2O_5-K_2O fertilizer. It contains 52% P_2O_5 and 34% K_2O and is Nitrogen-free (**Table 7**). MKP is the perfect instrument to control the so important nutrient balance between N, P and K. Using MKP offers the opportunity to give the most preferred N-source, but also to limit or avoid the use of Nitrogen in accordance to the crop's needs. Due to its high quality characteristics, MKP can be applied in hydroponic systems, in fertigation and/or as a foliar spray.

Fertigation with MKP

In continuous fertigation, the concentration of the nutrient solution should be between 0.5-1.5 g/l. For the mother solution, a concentration of 10-15 % can be used depending on the water temperature. The number of fertigation applications should be spread in the corresponding period of application.

Foliar application

MKP is compatible with the majority of pesticides and fertilizers in common use. However MKP should not be mixed with Calcium/Magnesium containing fertilizers. The trace elements Fe, Mn, Zn and Cu are only workable in a mix when they are protected/chelated. Due to its buffer action at pH 4.5 MKP can increase the life of the active ingredient of the pesticides.

The use of wetting agents is recommended only if MKP is applied without mixing with other products. An optional tank mix with 0.5-1% urea low buiret (U.L.B.) improves penetration. The best time to spray is the early morning or in the evening & when temperatures are lower. High temperature and low humidity increase the susceptibility of the plants to injury from sprayed chemicals. Crops under water stress conditions should not be sprayed. These recommendations are guidelines only. They should be adapted to local conditions, as differences of climate, sod type, temperature, crop variety, application method and irrigation systems occur.

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Recommended quantities are calculated to satisfy the needs for Phosphorus, and partially the need for Potassium.

Chemical and physical properties

Table 7 Physical and chemical properties of mono potassium phosphate

Analysis	Typical	Min.	Max.
P_2O_5	52.0%	51.0%	-
P	22.7%	22.3%	-
K_2O	33%	33.0%	34.0%
K	28.6%	28.2%	-
Cl	25.0 ppm	4.3%	4.7%
F	30.0 ppm	-	40.0 ppm
Fe	10.0 ppm	-	20.0 ppm
As	2.0 ppm	-	3.0 ppm
pH	4.4-4.6		
Moisture (1 hr, 105°C)	1%		1%
Water insolubles	0.3%		0.3%
Solubility @ 20 ^{o}C	36 g/100g water		
Bulk density	1.2 g/mμ		

Source: **Wenkem** (2012)

Potassium chloride (KCl) (International Plant Nutrition Institute, 2011)

The role of K as an Essential Nutrient for Plant Nutrition, Potassium is one of the essential plant nutrients found in high concentrations in plants. Potassium is assimilated through the roots as K^+ and always remains in this chemical form, unlike many other plant nutrients. It is present in the cell solution and serves as an activator

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of many cellular enzyme processes. Potassium has an essential role in photosynthesis, protein formation, nitrogen (N) fixation, starch formation, and energy transport.

Perhaps the most noted function of K in plants is the regulation of water relations and the proper function of leaf stomata. Potassium also plays an important role in improving the quality of harvested plant products and enhancing the plant's natural disease and insect resistance.

Mining Techniques for potash production

Potash is obtained by one of three methods: conventional shaft mining, solution mining, evaporation of surface brine.

The majority of global potash production occurs with conventional underground mining. Solution mining is more commonly used where ore deposits are irregular and deep.

Potassium chloride is by far the most common potash fertilizer source and often the least expensive. It is frequently referred to as muriate of potash (MOP) and contains between 60 to 63% K_2O; 46% Cl

Primarily mined as sylvinite ore containing KCl and NaCl, Milling and a floatation agent used to separate salts, Many colors and sizes available (**Figure 14**), Traces of iron oxide give some particles a reddish tint.



Figure 14 Many colors and sizes of potassium chloride

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Physical and Chemical Properties

Physical state and appearance: Solid. (White crystals)

Odor: Odorless

Taste: Saline. (Strong)

Molecular Weight: 74.55 g/mole

Color: White

pH (1% soln/water): ~7

Boiling Point: 1420°C (2588°F)

Melting Point: 770°C (1418°F)

Specific Gravity: 1.987 (Water = 1)

Solubility: 20 g in 100 g water 25°C, Very slightly soluble in methanol, n-octanol

Suspending agents

Properties of suspending agents

Suspending agents or thickening (swelling or gelling) agent is clays or other materials which, when added to aqueous liquid, swells and forms a gel, thereby increasing the viscosity of the liquid and enhancing its suspension properties and more water repellent. Clays are attapulgite, sepiolite and sodium bentonite. As the other materials are polysaccharides. They are dispersed and reflocculated in a suspension fertilizer and impart gel properties and a thixotropic character to the suspension fertilizer. These properties give maximum suspension when the suspension fertilizer is at rest. There are high apparent viscosities when the system is subjected to low and medium shear, and there are low apparent viscosities when the suspension is subjected to high shear. Such characteristics are desirable for the suspension fertilizer industry because when the suspension is stored, the gel will hold up the insoluble nutrients; under low shear conditions (pumping) the high apparent viscosity will hold the insoluble nutrients up while allowing the suspension to flow and be pumped. While under high shear conditions (spraying), the low apparent

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viscosity allows the suspension to be atomized into droplets for uniform application. To achieve these stabilizing effects, anywhere from 0.5 to 5% clay is incorporated into the mix (Wolf *et. al*., 1985).

For an experienced research, all of 3 clays are consisted of hydrated magnesium aluminum silicate and some sodium which may be released Mg, Al and Na in the suspension fertilizers. They will react with phosphate ion to form of phosphate salts. Attapulgite clays are widely used as suspending agent with some dispersants in suspension fertilizer plants (Anon, 1974; Scott *et. al*., 1978; Sawyer, 1975). Sepiolite is more reactive than attapulgite with the slightly acidic liquid phase of fertilizer suspensions (Wolf *et. al*., 1985) but the appropriated suspension fertilizers must have pH 6.5-8. Sodium bentonite is equally effective for use in non-acidic urea ammonium nitrate (UAN), ammonium orthophosphate (AOP) and ammonium polyphosphate (APP) suspensions but sodium bentonite cannot be dispersed into an ionized fluid fertilizer such as ammonium nitrate or ammonium phosphate (Salladay *et. al*., 1984).

Polysaccharides: Xanthan gum, one class of suspending agent is prepared from a carbohydrate which has been reacted with a microorganism of genus Xanthomonas (Fox and Oldland, 1976). A pseudo-cross-linked structure is obtained in water due to the form of Xanthan gum macromolecule and reversible interactions between these molecules even at low concentration. This phenomenon called gravitational stabilization by continuous phase structuration should avoid sedimentation and caking during long term storage of suspension fertilizers. They are widely used in many kinds of solid raw materials: urea, KCl, MKP, MAP, DAP and KNO_3 which are formulated in suspension fertilizers with pH 6.5-8. Furthermore, they are decomposed by micro-organisms in a field and are compatible with herbicide: paraquat (Colegrove, 1984).

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Xanthan gum, promising suspending agent

Origin

Since the original discovery of xanthan in the late 1950's and subsequent commercial production in the early 1960's there have been numerous studies to understand its functional and molecular properties (Kennedy and Bradshaw, 1984; Kang and Pettitt, 1993). The initial interest came from the Northern Regional Research Laboratories (NRRL, U.S. Department of Agriculture), where NRRL B-1459 was isolated as part of a wider screening program for new microbial polysaccharide entities. The NRRL were keen to find new functional polysaccharides to reduce supply and quality issues associated with seasonal, climatic, and skilled labour dependency of other plant sources. The US also had an overstock of corn starch, providing a plentiful supply of glucose for fermentation (Kennedy and Bradshaw, 1984). NRRL B-1459 became known as xanthan, and was shown to be a polysaccharide with three important properties (a) high viscosity at low concentration; (b) high pseudoplasticity and (c) insensitivity to variation in salt concentration, pH and temperature (Jeanes *et al*., 1961; Morris, 1977; Southwick *et al*., 1982).

Xanthan gum is a microbial exopolysaccharide produced by the naturally occurring bacterium *Xanthomonas campestris*. *X. campestris* was originally isolated from the cabbage plant, where it is responsible for black rot disease (Kennedy and Bradshaw, 1984). It is a widely used biopolymer in the food and pharmaceutical industries and is often used for the purposes of thickening, suspending, stabilising and gelling (Sutherland, 2001). Xanthan gum is also used in many other fields such as petroleum production, pipeline cleaning, enhanced oil recovery, textile printing and dyeing, ceramic glazes, slurry explosives and in cosmetics (Kang and Pettitt, 1993).

Xanthan is produced on an industrial scale by fermentation; in a well-aerated and principally carbohydrate medium containing other trace elements. It is precipitated from the fermentation broth using isopropyl alcohol, then dried and milled (Cottrell *et al*., 1980).

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In this research, a Xanthan gum is employed in the suspension fertilizer production method. It is a high molecular weight linear exocellular material. It has a molecular weight in excess of 200,000 preferably over 1 million DA (Fraley and Rogers, 1997). Xanthan gum has been used in industrial suspensions for about 20 years (Wolf *et. al*., 1985).

The structure of xanthan

The primary structure

Xanthan consists of a pentasaccharide repeating subunit consisting of two D-glucopyranosyl units, two D-mannopyranosyl units and a D-glucopyranosyluronic acid unit as determined by methylation analysis and uronic acid degradation (Jansson *et al*., 1975). The molecule has a (1 → 4) linked β -D-glucopyranosyl backbone, as is found in cellulose, but with a trisaccharide side chain attached to the O-3 position on alternate glucosyl units. The side chain is constructed such that the D-glucuronosyl unit is flanked by mannosyl units as shown in **Figure 15** (Jansson *et al*., 1975; Melton *et al*., 1976). Approximately half of the terminal D-mannosyl units have a pyruvic acid moiety bridging the O-4 and O-6 positions, the other D-mannosyl unit being substituted at the O-6 position with an acetal group (Kang and Pettitt, 1993). As a consequence of glucuronic acid in the side chain, xanthan is available as a sodium, potassium or calcium salt (Cottrell *et al*., 1980). Xanthan has been estimated to have a molecular weight between 2 - 50 x 10^{-6} Da. This wide range of values is believed to arise from polymer chain association (Dintzis *et al*., 1970).

The secondary structure

Polysaccharides which display interesting solution properties, tend to form ordered structures in the aqueous environment (Kennedy and Bradshaw, 1984). Rees (1972) made the first observations that xanthan existed in an ordered form using optical rotation. It was observed that with increasing temperature a sigmoidal change

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in optical rotation could be seen, suggesting a conformational change and order to disorder transition. Other studies using rheology, NMR relaxation, and circular dichroism all confirmed this initial theory (Holzwarth, 1976; Morris *et al*., 1977; Milas and Rinaudo, 1979). An increase in ionic strength has been shown to shift the transition point to higher temperatures, such that xanthan exists in the ordered form to temperatures above 100 ^{o}C (Morris, 1977).

X-ray diffraction studies have shown the molecular conformation to be a right handed 5-fold helix, in which the tri-saccharide side chains align with the backbone providing rigidity to the helix (Moorhouse *et al*., 1977). Numerous studies have been performed to elicit the exact conformation of xanthan however there is still no unanimous consensus. Some studies suggest a single helix (Holzwarth, 1976; Norton *et al*., 1984) whilst others propose a double helix (Holzwarth and Prestridge, 1977; Paradossi and Brant, 1982; Sato *et al.,* 1984; Gamini and Mandel, 1994). Electron microscopy of xanthan has been performed by Stokke and co-workers to further understand the conformation however this provided evidence of both conformations, making it difficult to generalise the secondary structure of xanthan (Stokke *et al*., 1986). Work by Young *et al*. (1994) was unable to distinguish between the single or double helix, but established that the helical ordered form is stabilized principally by hydrogen bonding (Young *et al*., 1994). Paoletti *et al.* (1983) have reported that the nature of the double helix is either side-by-side or intertwined but could not be determined. The model proposed by Norton *et al*. (1984) is shown in **Figure 16**.

The degree of acetylation and pyruvation is important for the stabilization of the ordered form (Gamini and Mandel, 1994). It is known that the acetate groups tend to promote the formation of the ordered form through hydrogen bonding, in contrast to the pyruvate groups which favour the disordered form as a result of electrostatic repulsion (Pelletier *et al*., 2001).

A significant number of polymers form random coils in solution. This is often referred to as the flexible chain model. In 1949 Kratky and Porod investigated an exception to this, the wormlike chain model. The details of the model are not essential

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here, however an important parameter used within it is known as *q* or the persistence length of the polymer chain. The importance of *q* is that it provides a description of chain stiffness and for flexible polysaccharides such as carboxymethylcellulose, *q* has been quoted of being between 8 and 30 nm. Xanthan however has values of *q* ranging from 100 - 300 nm indicating that the xanthan molecules form a long rigid rod in solution (Lapasin and Pricl, 1999), however there have also been suggestions that xanthan can be classed as semi-rigid chain (Holzwarth, 1981).

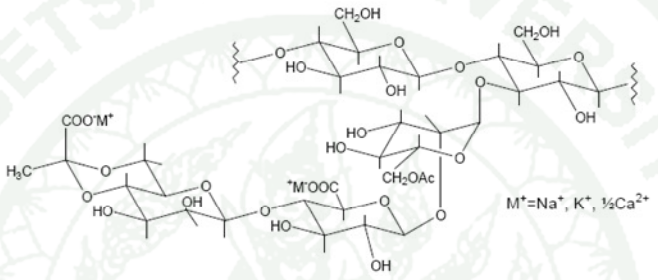

Figure 15 The primary structure of xanthan gum

Xanthan is made from a cellulose backbone with a trisaccharide side chain on alternate glucose residues. The side chain is made from a glucuronic acid residue flanked by two mannose residues (Jansson *et al.*, 1975). The terminal mannose is approximately 50% pyruvated, the other mannose having an acetal group.

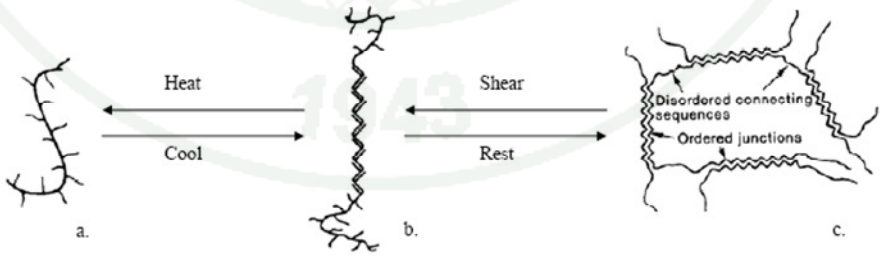

Figure 16 A diagrammatic representation of the order to disorder transitions in xanthan gum under the influences of temperature and shear. The long range ordered network (c.) is converted to a local ordered system (b.) by shear and then to the random coil (a.) by heat. Adapted from (Norton *et al.*, 1984)

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Solution properties

In an aqueous environment at low ionic strength, polyelectrolytes normally exist in a highly extended conformation and give rise to a high solution viscosity. Increasing temperature normally reduces the viscosity as a result of chain flexibility. Increasing ionic strength results in intramolecular charge screening, reducing the size of the polymer coil and resulting in a drop in the solution viscosity (Kennedy and Bradshaw, 1984).

Xanthan is soluble in both hot and cold water (Garcia *et al*., 2000). It exhibits high viscosity at a low concentration and maintains its viscosity in high ionic environments, indicating a departure from the normal random coil conformation. In some cases solution viscosity may increase with ionic strength (Whitcomb, 1978). Xanthan also maintains its viscosity in moderate ionic environments with increasing temperature. In low ionic environments there is an anomalous increase in viscosity with increasing temperature over a specific narrow range indicating a conformational change (Morris, 1977) but in general xanthan viscosity is independent of salt concentration above 0.1% salt (Kang and Pettitt, 1993). Under the influence of shear, xanthan is pseudoplastic and exhibits very low viscosity at high shear rates (Milas *et al*., 1985). These solution properties are directly related to the xanthan behaviour in solution, in which the rod-like helical chains entangle to form a complex network. The weak aggregation of the network results in the pronounced pseudoplasticity, however the high low shear viscosity is a result of helix rigidity. The addition of electrolytes reduces electrostatic repulsion allowing the side chains to align with the helical backbone and further promoting the helical conformation (Kang and Pettitt, 1993). The addition of divalent ions has been proposed to also improve coil-coil interactions by bridging carboxylate groups (Ross *et al*., 1983). The temperature stability can be attributed to the stability of the helical conformation.

There has been much debate over whether xanthan exhibits a yield stress. Early work suggested this to be true (Whitcomb *et al*., 1977), however using modern instrumentation it is now believed not to be the case.

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Xanthan, in the presence of salt is insensitive to pH over the range pH 2-10 (Sandford *et al.,* 1977). Deacetylation tends to occur above pH 9, however this has little effect on the its solution properties (Kang and Pettitt, 1993). At pH values below 3, deacetylation and depyruvation also occur, again having little effect on the solution properties (Callet *et al*., 1988; Garcia *et al.,* 2000).

Compatibility with other materials

Xanthan shows a remarkable level of compatibility with most substances. Xanthan is unaffected by enzymes such as protease, cellulase, hemicellulase, pectinase and amylase when in the ordered conformation, xanthan is however degraded by cellulase when promoted to the disordered form. Xanthan is also degraded by enzymes produced by some *Bacillus* species (Sutherland, 1995).

Xanthan is compatible with monovalent and most divalent salts and the viscosity is maintained at high salt concentrations. Polyvalent salts however do show compatibility issues. Salts such as aluminum (III) sulphate and lead (II) nitrate can cause gelation and precipitation over a wide pH range and salts such as copper (II) chloride, barium (II) chloride and iron (II) sulphate are incompatible above pH 10 (Cottrell *et al.,* 1980; Kang and Pettitt, 1993).

Xanthan dissolves directly in strong acids including 5% sulphuric acid and 10% hydrochloric acid. It also dissolves in strong alkalis such as 5% sodium hydroxide to yield thickened solutions. All of these solutions have good stability over several months. Xanthan is also compatible with a number of organic solvents such as methanol, ethanol, isopropanol and acetone up to concentrations as high as 50%. At concentrations higher than this gelation or precipitation occurs. Xanthan is however incompatible with peroxides (Challen, 1993; Kang and Pettitt, 1993).

Xanthan is also compatible with non-ionic surfactants up to concentrations of 20% and anionic surfactants up to 15%. At concentrations above these a salting out effect occurs (Cottrell et al., 1980).

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Uses of xanthan gum

From the description of the properties described above the reader will appreciate that xanthan gum is a most useful hydrocolloid. Since its discovery it has found many uses some of which will be discussed below. A number of key uses for xanthan are shown in **Table 8**.

Table 8 Some miscellaneous uses for xanthan gum

Application	Functionality Utilised	Reference
Textile printing	Xanthan is used for its thickening properties to prevent migration of dyes.	(Racciato 1976) (Cottrell et al., 1980)
Ceramic glazes	Xanthan is compatible with glaze components. It is able to control drying time and thereby reduced imperfections.	(Kang and Pettitt, 1993)
Cleaners	Xanthan is stable with acid and alkali. Its pseudoplasticity also allow easy application and then retention.	(Kang and Pettitt, 1993)
Slurry explosives	Xanthan is used to thicken nitrate based explosives as a result of its high compatibility with salts. This can be pumped into rock fissures or used in a canister form.	(Kang and Pettitt, 1993)
Agriculture	Xanthan is used for suspension of chemicals and to prevent drift. It also promotes cling for greater duration of action. Xanthan is also used in liquid feeds for its suspending properties.	(Andrew, 1977) (Cottrell et al., 1980)
Paints, Polishes and Inks	Xanthan is used for its thickening properties to prevent migration.	(Cottrell et al., 1980)

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Suitable properties of the selected solid raw materials

All of the information of the selected solid raw materials and the preliminary research in them results in compatible properties for suspension fertilizer process were listed in the **Table 9.**

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Table 9 The preliminary experiment resulted in physical properties of solid raw materials, xanthan gums and saturated solution

Raw materials	Physical property						Saturated solution		
	Color	Size	Molecular weight	pH[1/]	SG	Viscosity[2/] (mPa.s)	Solubility[3/]	SG[4/]	pH[5/]
Urea	white	granular (7-14 mesh)	60.0	7.53	-	-	119.9[6/]	1.154	7.92
MAP	white	fine crystal	115.0	4.53	-	-	38.0[7/]	1.136	4.04
MKP	white	fine crystal	136.1	4.96	-	-	26.0[7/]	1.119	4.46
KCl	white	fine crystal	74.0	6.75	-	-	20.0[7/]	1.116	7.14
Gum 2.5%	-	-		6.10	1.014	139	-	-	-
Gum 3.0%	-	-		6.04	1.016	167	-	-	-
Gum 5.0%	-	-		6.01	1.028	285	-	-	-

Note: [1/]1% in water 25°C, [2/]by Brookfield Viscometer in spindle # 2, 60 rpm and time 1 min, [3/] g/100 g water 25°C, [4/]specific gravity,
[5/] in saturated solution, [6/]effected on high density in the suspension,
[7/] effected on low density in the suspension

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Rheology

The term rheology is relatively recent and was first used in 1929 at the founding of the American Society of Rheology and was defined as *"the study of the deformation and flow of matter"* and is derived from the Greek word *Rheos* meaning 'stream' or 'anything flowing' and *ology* meaning study (Butterfield *et al.*, 2003). The concepts behind rheology were however studied far earlier by Robert Hooke in 1678, who developed the *"True theory of elasticity"* and also Isaac Newton in 1687, who published work on steady shearing flow (Barnes *et al.*, 1989).

Shear stress and shear strain

Consider the application of lateral force **F** to the surface of a cube as shown in **Figure 17**. The force per unit of area **A** is known as the shear stress (σ) and is measured in Pascals (Pa). This shear stress causes a resulting deformation Δ and a shear strain (γ), which can be defined by:

$$\gamma = \frac{\Delta}{d} \qquad (1.2)$$

where *d* is the distance between the top and bottom surfaces. As both Δ and *d* share the same units, strain is dimensionless. Where the body to which the force is applied is an elastic solid, the force will cause deformation, on removal of the force, the object will resume its original shape. Where the body is a viscous liquid the application of the force will result in flow of the liquid. The rate (velocity gradient) at which this liquid flows is known as the shear rate ($\dot{\gamma}$) and is defined by:

$$\dot{\gamma} = \frac{U}{d} \qquad \text{or} \qquad \dot{\gamma} = \frac{d\gamma}{dt} \qquad (1.3)$$

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where U is the relative velocity. Shear rate is measured in reciprocal seconds (s^{-1}) (Barnes *et al*., 1989).

Viscometry

Shear stress (σ) is proportional to shear rate as indicated in equation 1.4. Thus as the force increases so does the velocity of the liquid. The constant of proportionality for this relationship is known as viscosity (η), a measure of flow properties, and is measured in Pascal seconds (Pa.s).

$$\sigma = \eta\dot{\gamma} \qquad (1.4)$$

If the constant of proportionality viscosity, remains constant, the shear rate is directly proportional to the shear stress. This is known as Newtonian flow and is illustrated in **Figure 18a**. Fluids such as oils tend to exhibit Newtonian behavior as a result of the presence of only short range interactions and the lack of entanglement networks.

Not all materials behave as Newtonian fluids. There are three other principal types of rheological behaviour which are illustrated in **Figure 18**. **Figure 18b** shows a material which exhibits pseudoplastic flow. In this type of material there is a significant decrease in viscosity with increasing shear rate. These types of materials tend to be polymeric in nature exhibiting high viscosity at low shear rates as a result of the disruption of long range entanglement networks or rod-like molecules when the viscosity decrease is due to rods becoming aligned reducing the resistance to flow. Xanthan gum is a typical example of a pseudoplastic material. **Figure 18c** shows plastic behaviour. In this case, the flow curve can look similar to pseudoplastic flow however, there is a threshold shear stress which must be overcome before the fluid will flow. The material can be reversibly deformed, however above the threshold (yield stress) the material starts to flow as a result of structure breakdown. Examples of such materials include emulsions such as mayonnaises (Tabilo and Barbosa, 2005) or highly concentrated suspensions (Aulton, 1988; Lapasin and Pricl, 1999). The last

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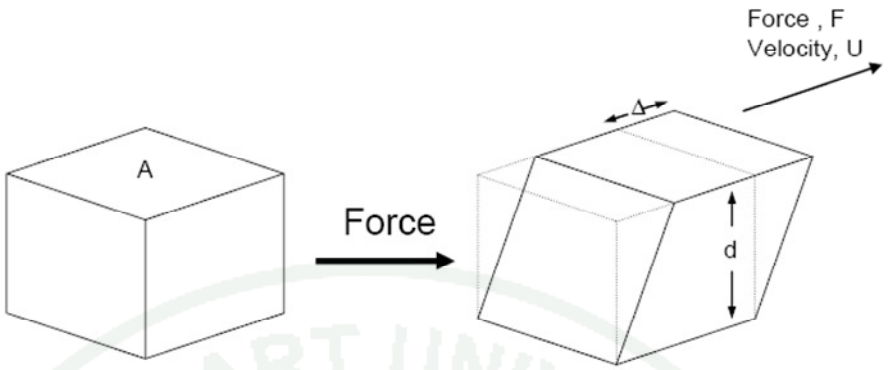

Figure 17 A diagrammatic representation of shear strain deformation. The force **F** is applied to the body over a given area **A**. This results in a deformation ?. (Adapted from Barnes et al., 1989)

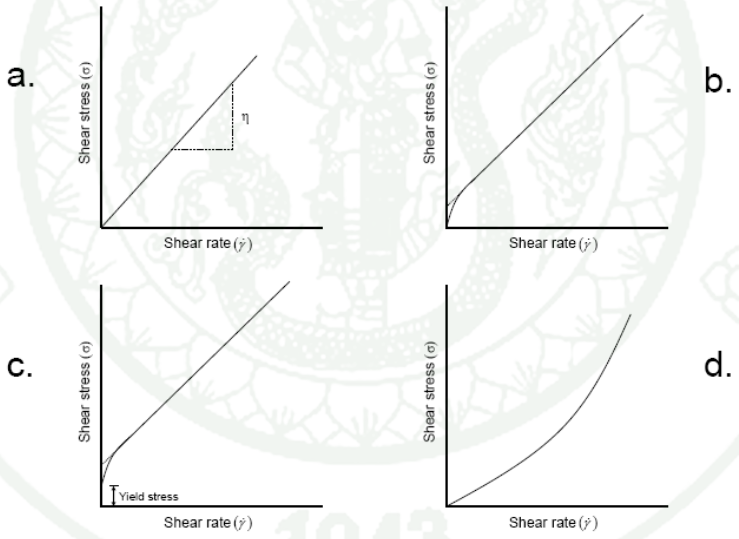

Figure 18 Diagrammatic representations of the four principal types of continuous shear behaviour exhibited by fluids. (a) Newtonian behaviour, (b) pseudoplastic behaviour, (c) plastic behaviour and, (d) dilatant behaviour. (Aulton, 1988; Florence and Attwood, 1988; Barnes et al., 1989)

type of fluid behaviour is that shown in **Figure 18d** and is known as dilatant flow or shear thickening. In this type of fluid the viscosity increases with increasing shear

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stress. This type of flow is far less common than the other three previously described and tends to occur in highly concentrated dispersions of small deflocculated particles.

At low shear the particles are free to move, and exhibit low viscosity. At high shear the particles aggregate thereby increasing the resistance to flow and hence the viscosity increases (Barnes et al., 1989). Apparent dilatancy can also be observed when laminar flow is superseded by turbulent flow; therefore care must be taken when interpreting flow data.

To assist in describing fluid behaviour a number of models have been proposed to describe shear flow (Lapasin and Pricl, 1999). The simplest model is the power-law model described by Ostwald and de Waele and is shown in equation 1.5 where K and n are constants.

$$\sigma = K\dot{\gamma}^n \tag{1.5}$$

The power law therefore states that for value of $n < 1$ the mixture shear thins, for values of $n > 1$ the fluid shear thickens. When n = 1 the fluid is Newtonian (cf. equation 1.4 which therefore makes $K = \eta$). The power law is simple and easy to apply and is often very useful in the middle shear rate region. Modern rheometers are able to obtain shear data over increasingly wide ranges, and often the power law becomes inadequate as viscosity often tends to asymptote to constant values as (the zero-shear viscosity, $\eta 0 \longrightarrow -\gamma\&_0$) and (the infinite shear viscosity, $\eta\infty \longrightarrow -\gamma\&_\infty$). To overcome these issues a number of models have been proposed such as the Cross model and the Carreau model. The Cross model is shown in equation 1.6 where λ describes the position of the power-law region on the shear rate scale.

$$\sigma = \eta_\infty \dot{\gamma} + \frac{(\eta_0 - \eta_\infty)\dot{\gamma}}{1 + (\lambda\dot{\gamma})^{1-n}} \tag{1.6}$$

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In addition, the presence of a yield stress can also be a problem. Equations such as the Herschel-Bulkley equation (1.7) take this into account by adding a parameter to describe the yield stress, σ_y.

$$\sigma = \sigma_y + K\dot{\gamma}^n \qquad (1.7)$$

Factors affecting viscosity

Whilst the characteristics of materials have a large impact on the type of flow behaviour, there are however other important factors which can affect the viscosity of a fluid.

Concentration

With the exception of the liquid crystalline transition mentioned previously, increasing the concentration of a polymer component in a solution will increase the viscosity. At low concentrations, molecules are sufficiently far apart in solution that their coils do not overlap and viscosity is approximately linearly related to concentration ($\eta \propto c^{1}$). At a critical overlap concentration, known as *c**, coils overlap and molecules entangle (Sworn, 2004). In this region $\eta \propto c^{3.5 - 4.0}$ (Lapasin and Pricl, 1999).

Temperature

Temperature can have pronounced effects on the viscosity of a fluid. Often with materials such as oils an elevated temperature will result in a significant decrease in viscosity as a result of intermolecular van der Waals bonds being reduced and hence raising molecular mobility. In the case of water a 1°C rise will result in a 3% decrease in viscosity, therefore to achieve a level of 1% accuracy, temperature must be controlled to within $\pm 0.3^{o}$C. Polymers also exhibit similar temperature effects as

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elevated temperatures can break intermolecular bonds such as hydrogen bonds. There are also systems which can increase in viscosity with increasing temperature. These tend to be fluids that gel as a result of heat, examples include methylcellulose and hydroxyl propyl methyl cellulose (Haque and Morris, 1993; Haque *et al*., 1993) which are both generally liquid at room temperature but gel on heating.

Shear rate

The effect of shear rate has been dealt with briefly when describing the types of flow behaviour. As a result of the different behaviour types shear rate can often play a significant role with both advantages and disadvantages. In the case of dilitant fluids an increase in the rate of flow will significantly enhance viscosity making pumping difficult. Pseudoplastic fluids such as xanthan show low viscosity at high shear rates making pumping easier.

Shear rate is different for different applications. **Table 10** shows some examples of common applications and their relative shear rates. It follows that pseudoplastic materials make ideal suspending agents as they exhibit high viscosity at low shear rates, particularly producing suspensions in a high shear mixer is relatively easy as the viscosity is greatly reduced at high shear rates.

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Table 10 Typical shear rates found in some common industrial settings

Situation	Typical shear rate range (s^{-1})	Application
Sedimentation of fine powders in a suspending liquid	10^{-6} - 10^{-4}	Medicines, paints
Leveling due to surface tension	10^{-2} - 10^{-1}	Paints, printing inks
Draining under gravity	10^{-1} - 10^{1}	Painting and coating. Toilet bleaches
Extruders	10^{0} - 10^{2}	Polymers
Chewing and swallowing	10^{1} -10^{2}	Foods
Dip coating	10^{1} -10^{2}	Paints, confectionary
Mixing and stirring	10^{1} -10^{3}	Manufacturing liquids
Pipe flow	10^{0} - 10^{3}	Pumping, blood flow
Spraying and brushing	10^{3} - 10^{4}	Spray-drying, painting, fuel atomization
Rubbing by hand	10^{4} -10^{5}	Application of creams and lotions to the skin
Milling pigments in fluid bases	10^{3} - 10^{5}	Paints, printing inks
High speed coating	10^{5} -10^{6}	Paper
Lubrication	10^{3} - 10^{7}	Gasoline engines

Source: Barnes *et al.* (1989)

Rheological effects

In all polymeric systems an initial increase in polymer concentration results in an increase in viscosity. For polymers that form liquid crystals, a point is reached where a further increase in concentration results in a decrease in viscosity (Onogi and Asada, 1980; Wissbrun, 1981; Sperling, 2001). This viscosity drop is primarily as a result of liquid crystal formation where molecules become aligned and optically anisotropic. This alignment often reduces the viscosity to less than that of an equivalent random coil of the same molecular weight, as a result of the reduced number of entanglements. Xanthan has also been shown to exhibit this type of

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behaviour (Oertel and Kulicke, 1991). The authors interpreted the viscosity changes in terms of the changes from a single phase, isotropic system to two phase mixed isotropic/anisotropic system, and then a single phase anisotropic system at high concentration (**Figure 19**). They interpreted the viscosity maximum as the inversion from anisotropic in isotropic, to isotropic in anisotropic in accordance with the work previously performed by Matheson (1980).

The maximum observed in viscosity has been shown in both continuous shear and dynamic oscillatory shear rheology where a maximum in both the elastic and viscous moduli are observed as a function of concentration (Lee and Brant, 2002a; Lee and Brant, 2002b)

Thixotropy (Reiner and Scott, 1967)

Thixotropy is the characteristic of a fluid to form a gelled structure over time when it is not subjected to shearing, and to liquefy when agitated.

Thixotropy is the property of some non-newtonian pseudoplastic fluids to show a time-dependent change in viscosity; the longer the fluid undergoes shear stress, the lower its viscosity. A thixotropic fluid is a fluid which takes a finite amount of time to attain equilibrium viscosity when introduced to a step change in shear rate. However, this is not a universal definition; the term is sometimes applied to pseudoplastic fluids without a viscosity/time component. Many gels and colloids are thixotropic materials, exhibiting a stable form at rest but becoming fluid when agitated.

It is important to note the distinction between a thixotropic fluid and a shear thinning fluid. The former displays a decrease in viscosity **over time at a constant shear rate,** while the latter displays decreasing viscosity with **increasing shear rate**. Fluids which exhibit the opposite property, in which shaking for a time causes solidification, are called rheopectic, sometimes called anti-thixotropic, and are much less common.

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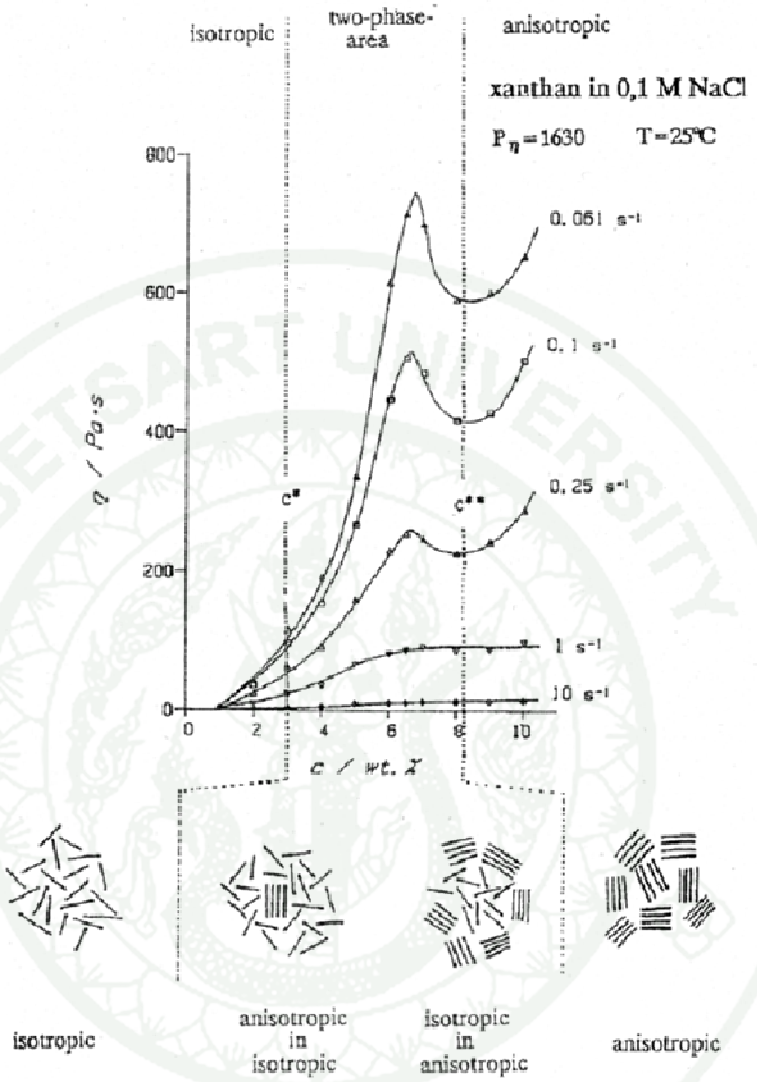

Figure 19 The viscosity of xanthan solutions as a function of concentration and shear rate (Taken from Oertel and Kulicke, 1991).

Some clays are thixotropic, with their behavior of great importance in structural and geotechnical engineering. In earthquake zones, clay-like ground can exhibit characteristics of liquefaction under the shaking of a tremor, greatly affecting earth structures and buildings. Similarly, a lahar is a mass of earth liquefied by a volcanic event, which rapidly solidifies once coming to a rest. Drilling muds used in geotechnical applications can be thixotropic. Landslides, such as those common in the

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cliffs around Lyme Regis, Dorset and in the Aberfan slag heap disaster in Wales are evidence of this phenomenon. Also honey from honey bees may exhibit this property under certain conditions.

Applications

Examples of applications for thixotropic fluids are the thickening of food stuffs and medical products. Toothpaste is thixotropic, which allows it to be squeezed out of the tube, yet retain a solid shape on the brush. Ketchup is frequently thixotropic.

Modern alkyd and latex paint varieties are often thixotropic and will not run off the painter's brush, but will still spread easily and evenly, since the gel-like paint "liquefies" when brushed out. Many clutch-type automatic transmissions use fluids with thixotropic properties, to engage the different clutch plates inside the transmission housing at specific pressures, which then changes the gear set.

Laponite, a mixture of water and synthetic clay, is used in the lubrication of robotic snails/slugs (gastropods), which rely on Laponite's thixotropic property for locomotion.

Etymology

The word comes from Greek *thixis*, touch (from *thinganein*, to touch) + *-tropy*, *-tropous*, from Greek *-tropos*, of turning, from *tropos*, changeable, from *trepein*, to turn.

Shear thinning

Shear thinning is an effect where a fluid's viscosity—the measure of a fluid's resistance to flow—decreases with an increasing rate of shear stress. Another name for a shear thinning fluid is a **pseudoplastic**. This property is found in certain

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complex solutions, such as lava, ketchup, whipped cream, blood, paint, and nail polish. It is also a common property of polymer solutions and molten polymers. Pseudoplasticity can be demonstrated by the manner in which squeezing a bottle of ketchup, a Bingham plastic, causes the contents to undergo a change in viscosity. The force causes it to go from being thick like honey to flowing like water. The study of such phenomena is called rheology.

All materials that are shear thinning are thixotropic, in that they will always take a finite time to bring about the rearrangements needed in the microstructural elements that result in shear thinning (Barnes, 1997)

isotropic and anisotropic

isotropic: Properties of a material are identical in all directions

anisotropic: Properties of a material depend on the direction; for example, wood. In a piece of wood, you can see lines going in one direction; this direction is referred to as "with the grain". The wood is stronger with the grain than "against the grain". Strength is a property of the wood and this property depends on the direction; thus it is anisotropic.

Van der Waals force

The fundamental difference between states of matter is the distance between particles. Because in the solid and liquid states Particles are closer together (**Figure 20**), they are as condensed phases.

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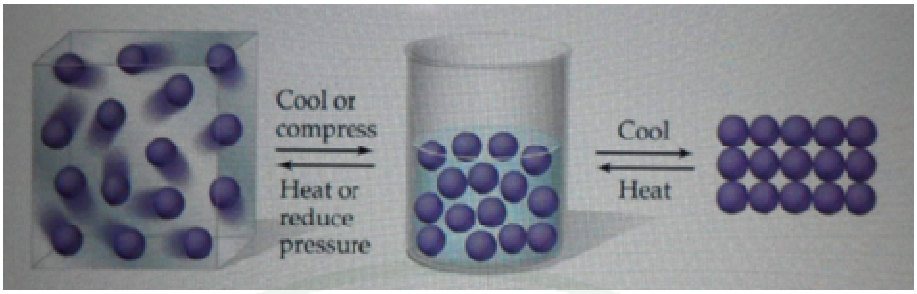

Gas (1) Liquid (2) Crystalline solid (3)

Figure 20 The state a substance is in at a particular temperature and pressure depends on two antagonistic entities: the kinetic energy of particles and the strength of the attractions between the particles. **Gas (1)**: total disorder; much empty space; particle have complete freedom of motion; particle far apart, **Liquid (2)**: disorder; particles or clusters of particles are free to move relative to each other; particles close together, **crystalline solid** (3): ordered arrangement; particles are essentially in fixed positions; particles close together

Intermolecular Forces

The attractions between molecules are not nearly as strong as the intramolecular attractions that hold compound together (**Figure 21**).

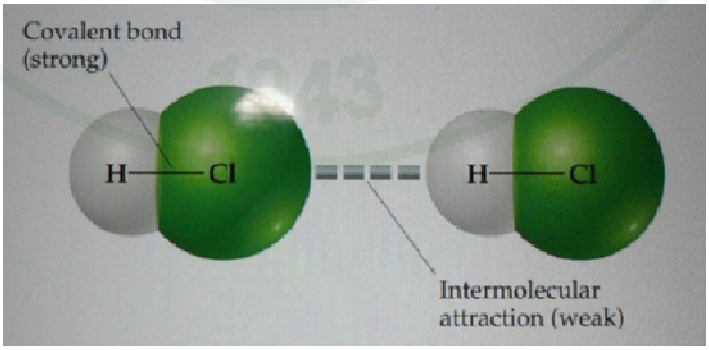

Figure 21 Covalent bond and intermolecular attraction

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They, however, strong enough to control physical properties such as boiling and melting points, vapor pressure, and viscosities. These intermolecular forces as a group are referred to as van der Waals forces which are:

Ion-dipole interactions
Dipole-dipole interactions
London dispersion forces or dispersion forces
Hydrogen bonding

Ion-dipole interactions are an important force in solution of ions. The strength of these forces are what make it possible for ionic substances to dissolve in polar solvents (**Figure 22**).

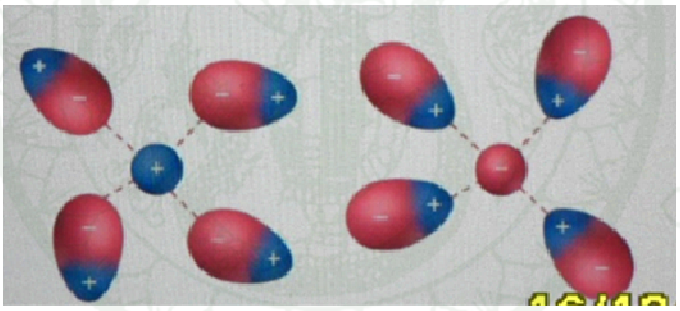

Figure 22 Cation-dipole attractions and anion-dipole attraction

Dipole-dipole interactions: molecules that have permanent dipoles are attracted to each other (**Figure 23**). The positive end of one is attracted to the negative end of the other and vice-versa. These forces are only important when the molecules are close to each other. The more polar the molecule, the higher is its boiling point.

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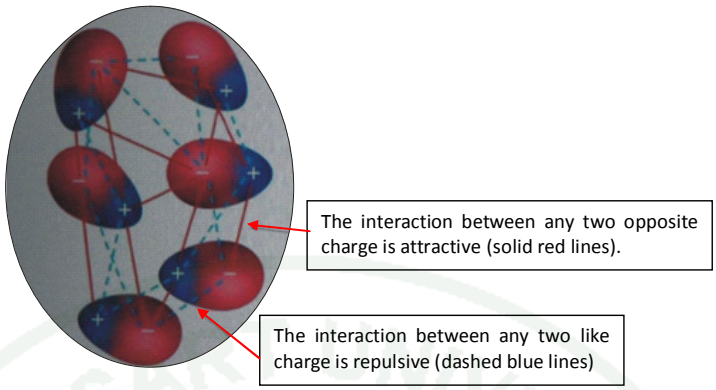

Figure 23 the attractive and repulsive between the intermolecular force

The more polar the molecule, the higher is its boiling point. While the electrons in the 1^s orbital of helium would repel each other (and, therefore, tend to stay far away from each other), it does happen that they occasionally wind up on the same side of the atom. At that instant, then, the helium atom is polar, with an excess of electrons on the left side and a shortage on the right side. Another helium nearby, then, would have a dipole induce in it, as the electrons on the left side of helium atom 2 repel the electrons in the cloud on helium atom1 (**Figure 24**)

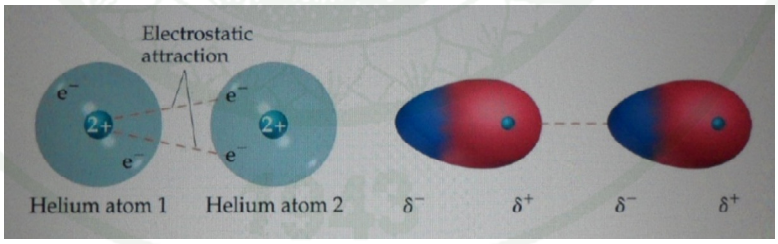

Figure 24 Dipole-dipole interactions in Helium atom

London dispersion forces, or dispersion forces, are attractions between an instantaneous dipole and an induced dipole. These forces are present in all molecules, whether they are polar or nonpolar. The tendency of an electron cloud to distort in this way is called polarizability.

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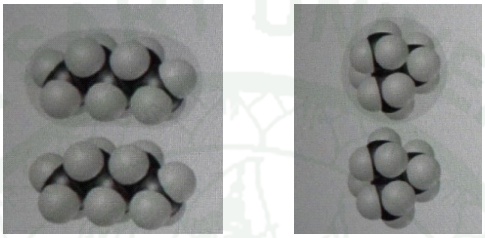
Factors affecting London Forces:

The shape of the molecule affects the strength of dispersion forces: long, skinny molecules (like *n*-pentane) tend to have stronger dispersion force than short, fat ones (like neopentane) (**Figure 25**). This is due to the increased surface area in *n*-pentane.



n-Pentane (bp = 309.4 K)

Neopentane (bp = 282.7 K)

Figure 25 The shape of the molecule affects the strength of dispersion forces

The strength of dispersion forces tends to increase with increased molecular weight. Large atoms have larger electron clouds, which are easier to polarize (**Figure 26**).

	Weight (amu)	Point (K)	Gas	Weight (amu)	Point (K)
F_2	38.0	85.1	He	4.0	4.6
Cl_2	71.0	238.6	Ne	20.2	27.3
Br_2	159.8	332.0	Ar	39.9	87.5
I_2	253.8	457.6	Kr	83.8	120.9
			Xe	131.3	166.1

Figure 26 The molecular weight tend to the strength of dispersion forces

Hydrogen bonding

The dipole-dipole interactions experienced when H is bonded to N, O, or F are unusually strong. These interactions are hydrogen bonds. Hydrogen bonding arises in part from the high electro-negativity of nitrogen, oxygen, and fluorine. Also, **when**

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hydrogen is bonded to one of those very electro-negative elements, the hydrogen nucleus is exposed (**Figure 27**)

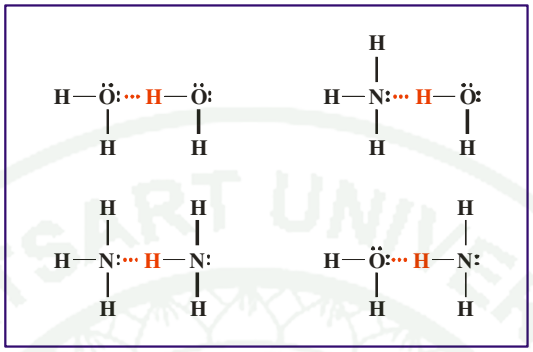

Figure 27 Hydrogen bonds in H_2O and NH_3

Intermolecular forces affect many physical properties:

The strength of the attractions between particles can greatly affect the properties of a substance or solution.

Viscosity

Resistance of a liquid to flow is called **viscosity.** It is related to the ease with which molecules can move past each other. Viscosity increases with stronger intermolecular forces and decreases with high temperature.

Surface tension

Surface tension results from the net inward force experienced by the molecules on the surface of a liquid.

Boiling point

The more polar the molecule, the higher is its boiling point.

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Hydrocolloids

A **hydrocolloid** is defined as a colloid system wherein the colloid particles are hydrophilic polymers dispersed in water. A hydrocolloid has colloid particles spread throughout water, and depending on the quantity of water available that can take place in different states, e.g., gel or sol (liquid). Hydrocolloids can be either irreversible (single-state) or reversible. For example, agar, a reversible hydrocolloid of seaweed extract, can exist in a gel and solid state, and alternate between states with the addition or elimination of heat.

Many hydrocolloids are derived from natural sources. For example, agar-agar and carrageenan are extracted from seaweed, gelatin is produced by hydrolysis of proteins of bovine and fish origins, and pectin is extracted from citrus peel and apple pomace. Gelatin desserts like jelly or Jell-O are made from gelatin powder, another effective hydrocolloid. Hydrocolloids are employed in food mainly to influence texture or viscosity (e.g., a sauce). Hydrocolloid-based medical dressings are used for skin and wound treatment.

Other main hydrocolloids are xanthan gum, gum arabic, guar gum, locust bean gum, cellulose derivatives as carboxymethyl cellulose, alginate and starch. Based on the nature of interaction between the dispersed phase and the dispersion medium, colloids can be classified as: Hydrophilic colloids: These are water-loving colloids.The colloid particles are attracted toward water. They are also called reversible sols. Hydrophobic colloids: These are opposite in nature to hydrophilic colloids. The colloid particles are repelled by water. They are also called irreversible sols.

Interaction between particles

The following forces play an important role in the interaction of colloid particles:

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Excluded volume repulsion: This refers to the impossibility of any overlap between hard particles.

Electrostatic interaction: Colloidal particles often carry an electrical charge and therefore attract or repel each other. The charges of both the continuous and the dispersed phase, as well as the mobility of the phases are factors affecting this interaction.

van der Waals forces: This is due to interaction between two dipoles that are either permanent or induced. Even if the particles do not have a permanent dipole, fluctuations of the electron density gives rise to a temporary dipole in a particle. This temporary dipole induces a dipole in particles nearby. The temporary dipole and the induced dipoles are then attracted to each other. This is known as van der Waals force, and is always present (unless the refractive indexes of the dispersed and continuous phases are matched), is short-range, and is attractive.

Entropic forces: According to the second law of thermodynamics, a system progresses to a state in which entropy is maximized. This can result in effective forces even between hard spheres.

Steric forces between polymer-covered surfaces or in solutions containing non-adsorbing polymer can modulate interparticle forces, producing an additional steric repulsive force (which is predominantly entropic in origin) or an attractive depletion force between them. Such an effect is specifically searched for with tailor-made superplasticizers developed to increase the workability of concrete and to reduce its water content.

Stabilization (peptization)

The stability of a colloidal system is the capability of the system to remain as it is. Stability is hindered by aggregation and sedimentation phenomena, which are driven by the colloids tendency to reduce surface energy. Reducing the interfacial tension will stabilize the colloidal system by reducing this driving force (**Figure 28**).

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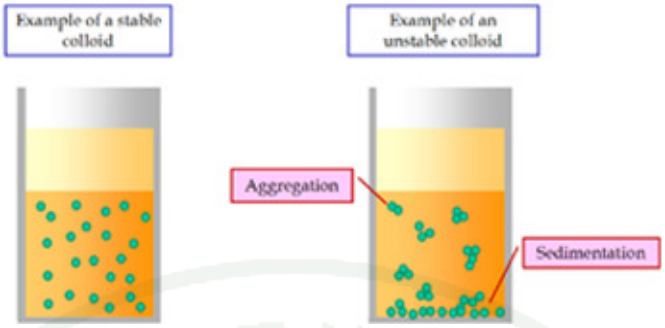

Figure 28 A stable and an unstable colloidal dispersion

Aggregation is due to the sum of the interaction forces between particles (Menachem *et al*., 1998; Israelachvili, 1991). If attractive forces (such as van der Waals forces) prevail over the repulsive ones (such as the electrostatic ones) particles aggregate in clusters.

Electrostatic stabilization and steric stabilization are the two main mechanisms for stabilization against aggregation.

Electrostatic stabilization is based on the mutual repulsion of like electrical charges. In general, different phases have different charge affinities, so that an electrical double layer forms at any interface. Small particle sizes lead to enormous surface areas, and this effect is greatly amplified in colloids. In a stable colloid, mass of a dispersed phase is so low that its buoyancy or kinetic energy is too weak to overcome the electrostatic repulsion between charged layers of the dispersing phase.

Steric stabilization consists in covering the particles in polymers which prevents the particle to get close in the range of attractive forces.

A combination of the two mechanisms is also possible (electrosteric stabilization). All the above mentioned mechanisms for minimizing particle aggregation rely on the enhancement of the repulsive interaction forces. Electrostatic and steric stabilization do not directly address the sedimentation/floating problem.

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Particle sedimentation (and also floating, although this phenomenon is less common) arises from a difference in the density of the dispersed and of the continuous phase. The higher the difference in densities, the faster the particle settling is.

The **gel network stabilization** represents the principal way to produce colloids stable to both aggregation and sedimentation (Comba, 2009; Cantrell *et al.*, 1997). The method consists in adding to the colloidal suspension a polymer able to form a gel network and characterized by shear thinning properties. Examples of such substances are xanthan and guar gum (**Figure 29**).

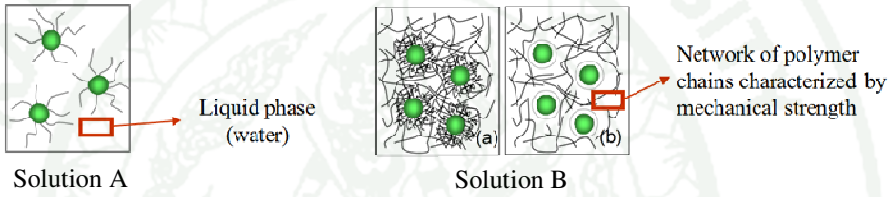

Figure 29 Solution A: steric stabilization and solution B: dispersion in gel network

Steric and Gel network stabilization

Particle settling is hindered by the stiffness of the polymeric matrix where particles are trapped (Comba, 2009). In addition, the long polymeric chains can provide a steric or electrosteric stabilization to dispersed particles.

The rheological shear thinning properties find beneficial in the preparation of the suspensions and in their use, as the reduced viscosity at high shear rates facilitates de-agglomeration, mixing and in general the flow of the suspensions.

Destabilization (flocculation)

Unstable colloidal dispersions can form flocs as the particles aggregate due to interparticle attractions. In this way photonic glasses can be grown. This can be

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accomplished by a number of different methods:

Removal of the electrostatic barrier that prevents aggregation of the particles, this can be accomplished by the addition of salt to a suspension or changing the pH of a suspension to effectively neutralize or "screen" the surface charge of the particles in suspension. This removes the repulsive forces that keep colloidal particles separate and allows for coagulation due to van der Waals forces.

Addition of a charged polymer flocculant, polymer flocculants can bridge individual colloidal particles by attractive electrostatic interactions. For example, negatively-charged colloidal silica or clay particles can be flocculated by the addition of a positively-charged polymer.

Addition of non-adsorbed polymers called depletants that cause aggregation due to entropic effects.

Physical deformation of the particle (e.g., stretching) may increase the van der Waals forces more than stabilization forces (such as electrostatic), resulting coagulation of colloids at certain orientations.

Unstable colloidal suspensions of low-volume fraction form clustered liquid suspensions, wherein individual clusters of particles fall to the bottom of the suspension (or float to the top if the particles are less dense than the suspending medium) once the clusters are of sufficient size for the Brownian forces that work to keep the particles in suspension to be overcome by gravitational forces. However, colloidal suspensions of higher-volume fraction form colloidal gels with viscoelastic properties. Viscoelastic colloidal gels, such as bentonite and toothpaste, flow like liquids under shear, but maintain their shape when shear is removed. It is for this reason that toothpaste can be squeezed from a toothpaste tube, but stays on the toothbrush after it is applied.

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Gravitational force (Marshall Middle School, 2013)

Gravity is **a force of attraction between objects.** When the molecules of one object pull on the molecules of another object. That pull is gravity at work. All matter is affected by gravity. Matter is anything that has mass and volume. Since all matter has mass, all matter is affected by gravity. Gravity (**gravitational force**) **pulls objects towards each other.** It acts on anything with mass. This is because the mass of most objects is too small to cause an attraction large enough to cause the objects to move towards each other. Even though gravity is "pulling" the pencil you're holding, its mass is so small that it's not really moving. There is, however, one object that is big enough to cause a noticeable attraction. That's right, the Earth! Earth has an enormous mass and thus an enormous gravitational force. When the Earth spins and gravity pulls on the clouds, weather can be affected. The Earth's gravity even holds the atmosphere close to our surface.

The Law of Universal Gravitation (**Figure 30**)

This law states: All objects in the universe attract each other through gravitational force.

The size of the gravitational force depends on two things:

Mass of the objects

Distance between the objects

The formula for this law is:

$$F = G \times \frac{m_1 \times m_2}{r^2}$$

F = force

G = gravitational constant = 6.673×10^{-11} Nm^2/kg^2 - always an uppercase G, do not confuse with g, which is for gravity

M = objects' mass

R = distance between objects

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Basically, there are two major parts to this law:

1. Gravitational force increases as mass increases
2. Gravitational force decreases as distance increases

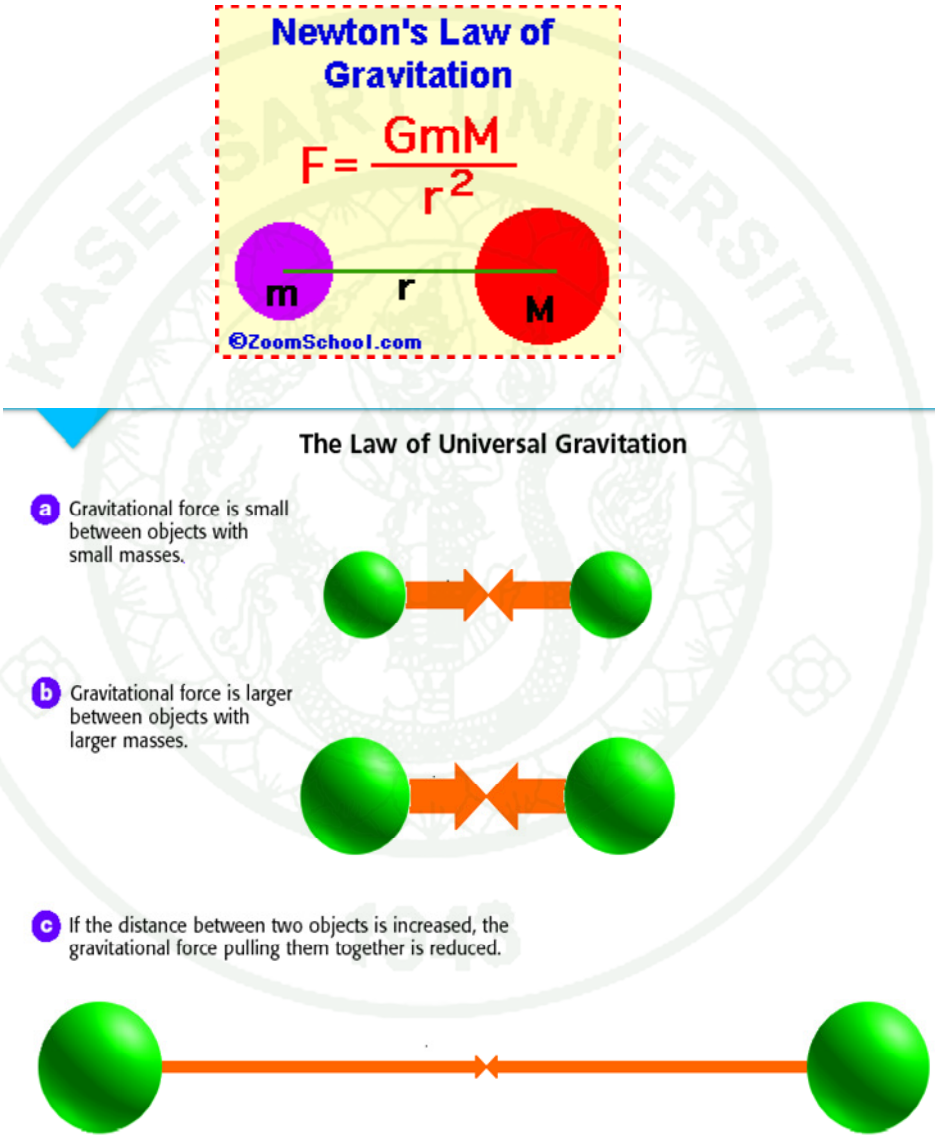

Figure 30 Newton's Law of gravitation and the Law of Universal Gravitation

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What is weight?

Weight is a measure of the gravitational force exerted on an object. Most of the time, when we're talking about weight, we're referring to the *Earth's* gravitational force on an object. Since gravity is a force and weight is a measure of gravity, weight is expressed in newtons (N). On Earth, a 100 gram object would weigh 1 N.

What is mass?

Mass is the amount of matter in an object. This does not change… ever! Whereas weight changes when gravity changes, mass always remains the same. Remember, mass is measured with a balance, where the mass of one object is compared to another object. On Earth, mass and weight are both constant since gravity is a constant force, which is why they seem like the same thing to us (**Figure 31**).

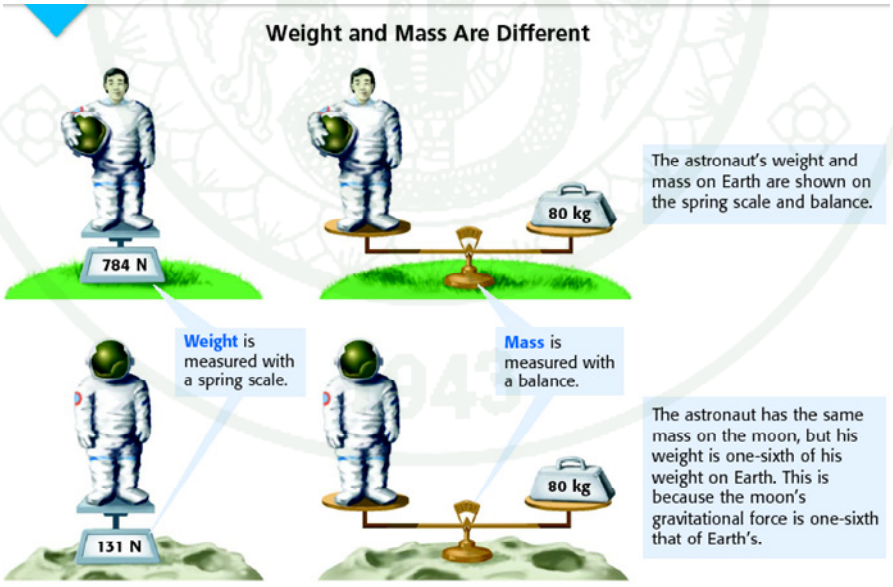

Figure 31 Comparison between weight and mass

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Solutions (BSE, 2012)

A **solution** is a homogenous mixture of two or more substances evenly distributed in each other. **Solutes** are the substances dissolved**. Solvent** is the liquid material in which the solute has dissolved. These are the components of a solution. The solute can be in the form of solid, liquid, or gas.

In terms of phase, a solution can be classified as gaseous, solid or liquid. Air is an example of a **gaseous solution**. It is the combination of nitrogen, oxygen, and carbon dioxide gases. Certain alloys such as brass (solution of zinc and copper) and coinage silver (solution of copper and silver) are examples of **solid solutions**. Seawater and blood are examples of **liquid solutions**.

Solutions are also classified as dilute and concentrated based on the relative amounts of components of the solution. When the solute is present in small amounts, the solution is said to be **dilute**. But when the solute is present in considerably significant amounts, the solution is said to be **concentrated**.

However, solutions must not be confused with **suspensions**. A basic example of suspension is the sand mixed with water as was shown in our activity. As you can see, the sand is not dissolved in water; it is merely suspended in it. The suspension produced is not also clear; it is actually opaque. And upon standing, you can see that the sand is slowly settling. In this regard, the composition of suspension is actually changing as the sand settles in, so it is a heterogenous mixture, unlike that of the solution. Also, when the clay particles are allowed to pass through the improvised filter paper, the sand is left behind. This is because the particles of a suspension are too large to pass through the filter paper, or through a membrane with finer openings.

Get a glass of water and put a pinch of powder dye. Observe the pattern of the movement of dye in water. What you just did best describes the dissolution process which fascinates chemists for years. The dissolution process is due to intermolecular forces (forces that exist between molecules). When two molecules overcome the

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attractive forces that exist between them, they absorb energy. On the other hand, when the attractive force is formed between two molecules, they release energy. Thus, we can say that dissolution process involves the absorption (endothermic) and release (exothermic) of energy. When the energy absorbed is greater than the energy released, the dissolution process is endothermic. The opposite scenario is true for exothermic process.

Solubility is the measure of how much solute will dissolve in a solvent at a specific temperature. The famous saying "like dissolves like" is important in predicting the solubility of a substance in a given solvent. This expression means that when two substances of same intermolecular forces and magnitude are mixed, they are likely to be soluble to one another. Take for example salt (NaCl) and water (H_2O) which are both polar. When these two substances are mixed, the attraction between NaCl and H_2O molecules has the same magnitude to the forces between NaCl molecules and between H_2O molecules. However, solubility is often confused with miscibility. **Miscibility** is the term used when two liquids are completely soluble with one another in all proportions while solubility is the term used when a solid or gas is completely soluble in liquid in all proportions. For example, alcohol and water are miscible to one another.

Factors Affecting Solubility of a Solute

A. Temperature

Temperature affects the solubility of substances. The solubility of a solid in liquid usually increases with increasing temperature since most dissolution process that involves a solid solute over a liquid solvent is endothermic. However, in the case of the solubility of gas in liquid, increasing the temperature will usually result to decrease in solubility.

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B. Nature of Solvent

The ability of a solute to be dissolved in a given solvent is affected by the type of bond of both the solute and solvent. In general, polar liquids dissolve polar compounds and the same is true with nonpolar liquids. Thus goes the saying "like dissolves like". This is the guiding rule in preparing solutions. Since water is a polar liquid, it dissolves polar compounds such as sugar ($C_6H_{12}O_6$) and salt (NaCl). Sometimes, in spite of all attempts, a substance does not appreciably dissolve in water even though it is polar. These substances are called insoluble salts (Table 11)

Table 11 Water solubility of common salts and bases

Soluble	Insoluble
Sodium salt	Carbonates (except sodium, potassium and ammonium)
Potassium salt	Phosphates (except sodium, potassium and ammonium)
Ammonium salt	Sulfides (except sodium, potassium and ammonium)
Acetates	Hydroxides (except sodium, potassium and ammonium)
Nitrates	
Chlorides (except silver, lead and mercury)	
Sulfates (except calcium, barium and lead)	

C. Pressure

The effect of pressure on the solubility of a solid or liquid solute is not as noticeable as that of a gaseous solute. The solubility of gases in water usually increases with increasing pressure. This relationship is first noticed by William

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Henry(1775-1836) in 1803 and its law is called after his name: **Henry's law or Pressure-Solubility Law**. This law states that in a given temperature, the mass of a gas that dissolves in a given volume of liquid is directly related to its pressure.

An example is the carbon dioxide gas dissolved in carbonated drinks. If the bottle is closed, the carbon dioxide gas remains dissolved in the beverage due to considerable amount of partial pressure present. But if it is opened, the pressure is released and carbon dioxide gas bubbles off the liquid due to a decrease in gas solubility.

Factors Affecting the Rate of Dissolution

A. Surface area

Surface area does not affect the amount of solute that will dissolve, but it does affect the solute's rate of dissolution. Thus, in order to make a solid solute dissolve faster, we frequently powder it, thereby increasing the surface area. This is why powdered coffee dissolves faster than granulated coffee even without stirring.

B. Rate of Stirring

The rate at which a solute dissolves can be increased by stirring the mixture. This process brings fresh solvent into contact with the solute and so permits a faster rate of dissolution.

C. Temperature

Generally, solubility increases with increasing temperature for most cases of solid in liquid. The increase in temperature causes an increase in kinetic energy of the solute, solvent and the solution thus facilitating rapid interaction with one another.

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Saturated, Unsaturated and Supersaturated Solutions

Solutions can also be classified as saturated, unsaturated and supersaturated. When a small amount of sugar is mixed in a glass of water, all the sugar will dissolve. If more and more sugar is added while stirring, a point is reached when some sugar will settle at the bottom of the glass even with continued rapid stirring. This type of solution is said to be saturated. Thus, a saturated solution is one that contains as much of the solute as it can hold at a given temperature. An unsaturated solution contains less solute than it has the capacity to dissolve.

The third type, the supersaturated solution contains more solute than is present in a saturated solution. This is a rather unstable condition. In this case, the excess solid will eventually separate from the solution as a precipitate in a process known as precipitation or as crystals in a process known as crystallization. Crystals have bigger granules than precipitate. Tawas or alum crystals are prepared as supersaturated solutions.

Nucleation and Crystal growth (Sundoc, 2012)

Crystallization is a separation and purification technique employed to produce a wide variety of materials. Crystallization may be defined as a phase change in which a crystalline product is obtained from a solution. A solution is a mixture of two or more species that form a homogenous single phase. Solutions are normally thought of in terms of liquids; however, solutions may include solids suspension. Typically, the term solution has come to mean a liquid solution consisting a solvent, which is a liquid, and a solute, which is a solid, at the conditions of interest. The solution to be ready for crystallization must be supersaturated. A solution in which the solute concentration exceeds the equilibrium (saturated) solute concentration at a given temperature is known as a supersaturated solution. There are four main methods to generate Super-saturation that are the following:

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- Temperature change (mainly cooling)
- Evaporation of solvent
- Chemical reaction and
- Changing the solvent composition (e.g. salting out).

The Ostwald-Miers diagram shown in **Figure 32**, illustrates the basis of all methods of solution growth. The solid line represents a section of the curve for the solute / solvent system. The upper dashed line is referred to as the super-solubility line and denotes the temperatures and concentration where spontaneous nucleation occurs.

The diagram can be evaluated on the basis of three zones:

• The stable (unsaturated) zone where crystallization is impossible,

• The metastable (supersaturated) zone where spontaneous nucleation is improbable but a crystal located in this zone will grow and

• The unstable or labile (supersaturated) zone where spontaneous nucleation is probable and so the growth.

Crystallization from solution can be thought of as a two step process. The first step is the phase separation, (or birth), of a new crystals. The second is the growth of these crystals to larger size. These two processes are known as **nucleation** and **crystal growth,** respectively. Analysis of industrial crystallization processes requires knowledge of both nucleation and crystal growth.

The birth of a new crystal, which is called nucleation, refers to the beginning of the phase separation process. The solute molecules have formed the smallest sized particles possible under the conditions present. The next stage of the crystallization process is for these nuclei to grow larger by the addition of solute molecules from the supersaturated solution. This part of the crystallization process is known as crystal growth. Crystal growth, along with nucleation, controls the final particle size distribution obtained in the system. In addition, the conditions and rate of crystal

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growth have a significant impact on the product purity and the crystal habit. An understanding of the crystal growth theory and experimental techniques for examining crystal growth from solution are important and very useful in the development of industrial crystallization processes. The many proposed mechanisms of crystal growth may broadly be discussed under a few general headings:

- Surface energy theories
- Adsorption layer theories
- Kinematic theories
- Diffusion - reaction theories
- Birth and spread models

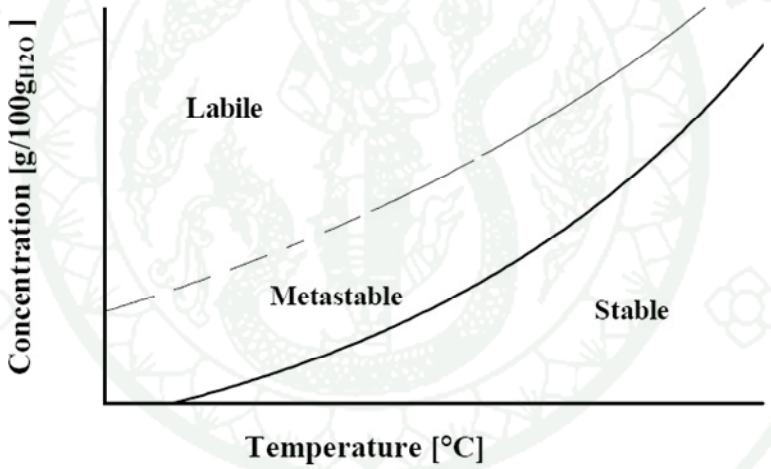

Figure 32 Ostwald-Miers diagram for a solute/solvent system

Mechanics of nucleation (Wikipedia, 2011)

Heterogeneous nucleation: Heterogeneous nucleation occurs much more often than homogeneous nucleation. It forms at preferential sites such as phase boundaries or impurities like dust and requires less energy than homogeneous nucleation. At such preferential sites, the effective surface energy is lower, thus diminishing the free energy barrier and facilitating nucleation. Surfaces promote nucleation because of

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wetting – contact angles greater than zero between phases encourage particles to nucleate. The free energy needed for heterogeneous nucleation is equal to the product of homogeneous nucleation.

When sugar is supersaturated in water nucleation will occur, allowing sugar molecules to stick together and form large crystal structures.

Nucleation normally occurs at nucleation sites on surfaces contacting the liquid or vapor**.** Suspended particles or minute bubbles also provide nucleation sites. This is called heterogeneous nucleation. Nucleation without preferential nucleation sites is homogeneous nucleation. Homogeneous nucleation occurs spontaneously and randomly, but it requires superheating or supercooling of the medium. Nucleation is involved in such processes as cloud seeding and in instruments such as the bubble chamber and the cloud chamber.

Supersaturation is a state of a solution that contains more of the dissolved material than could be dissolved by the solvent under normal circumstances. It can also refer to a vapor of a compound that has a higher (partial) pressure than the vapor pressure of that compound.

Chinese kale (Phakkhana)

Chinese kale was selected as the representative vegetable for growth enhancement, as it is the most popular vegetable in terms of consumption and has high nutritional value, especially calcium (Ca), phosphorus (P), and vitamin C. Chinese Kale (Chinese flowering broccoli, Kailaan, Gai lum, Phakkhana) is a brassica vegetable (*Brassica oleracea* var. *alboglabra*).

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Cultivars: Varieties differ in stem length and colour, from light to medium green (Cantwell *et al.,* 1996). The F1 hybrid varieties generally grow more vigorously (Moore and Morgan, 1998).

Soil type: Kailaan requires a fertile soil with good drainage and a high level of organic matter (Moore and Morgan, 1998).

pH: The optimum pH is between 6.0 and 7.0. It should not be allowed to fall below 5.0 (Moore and Morgan, 1998).

Temperature: The optimum temperature for rapid growth is 18-28ºC. Low temperatures promote early flowering and are necessary for complete floral development. The crop is frost tolerant and more heat tolerant than other broccoli (Sagwansupyakorn, 1994).

Plant density: A planting layout of 2-4 rows per bed and 8-12 cm between plants gives a density of 108 000 to 220 000 plants/ha (Cantwell *et al.,* 1996). Sow heavily and then thin after 3 weeks of growth. Thinned plants can be sold as the first harvest (Sagwansupyakorn, 1994). Dense planting results in a high leaf area index, a desirable product and high marketable yield. It also increases time to maturity and reduces the stem mineral content, due to higher competition among plants (Moore and Morgan, 1998). Seeds are sown at about 0.6 cm depth (Moore and Morgan, 1998). There are approximately 200 seeds/g.

Germination: The optimum temperature for germination is 25-30ºC (Sagwansupyakorn, 1994). Emergence occurs 3-6 days in summer and 4-10 days in autumn (Moore and Morgan, 1998).

Transplants: Seedlings are transplanted at 3-4 weeks (Moore and Morgan, 1998). Seedlings often grow too fast in polyhouses, causing early flowering and minimal vegetative production. Growth should be monitored, particularly in warm

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weather. Seedling trays require wind protection but should only be stored in polyhouses in cool weather.

Fertiliser: A number of fertiliser regimes are discussed in Moore and Morgan, (1998). High planting densities require higher levels of N, of 400 kg/ha or more (Hill, 1990). One format is a base dressing of 500 kg/ha Pivot 800, followed by side dressings of 125 kg/ha CaNO3 or equivalent at 3 weeks after transplanting. Dual (metalochlor) at 3 L/ha is often applied directly after transplanting.

Watering: The crop requires frequent light watering for optimum growth, since it is shallow rooted (Moore and Morgan, 1998).

Harvest: The crop is ready to harvest at 10 weeks from sowing in autumn and 8-9 weeks in summer (Moore and Morgan, 1998). Young flowering stems are selected with compact florets and small leaves attached, and cut at 15 to 20 cm length (Anonymous, 1997) with a sharp knife. Flavor is maximized when plants are harvested well before the buds begin to open. They should be harvested frequently to prevent bolting and toughening, particularly in summer. About three cuts can be obtained from one stem, and the main stalk should be cut relatively short to enhance further growth. A liquid feed after each harvest may benefit re-growth (Moore and Morgan, 1998).

Yield: The average yield in a season with 2-3 harvests is 6-11 t/ha (Shuler, 1995). Yield is dependent on harvesting frequency and method (Sagwansupyakorn, 1994).

Shelf life: A shelf life of more than 21 days is possible with the correct storage. This can be increased to 27 days by removing ethylene. Shelf life at 5-10ºC is reduced to 7-14 days (Wills *et al.,* 1999).

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MATERIALS AND METHODS

The research was taken place at the research laboratory of Captain Fertilizer Co. Ltd. Bangkok, Thailand, during December, 2012 to November, 2013. It consisted of 5 experiments as following.

Experiment 1: Effects of particle size of solid raw materials and speeds of agitator on production method of 25-7-7 analysis grade of suspension fertilizer

Experiment 1 was aimed to investigate the effects of 2 particle sizes of raw materials (>20 meshes milled size and 7-14 meshes original size) and 3 speeds of agitator (2620, 1280 and 620 rpm) on the solubility of each raw materials with fixed 3% xanthan gum. **Table 9** showed the preliminary experiment resulted in physical properties of solid raw materials, xanthan gums and saturated solution. The optimum particle size and speeds of agitator would be used as fixed factors in the experiment 2.

The experiment was designed for 2x3 factorial in CRD: 2 particle sizes of raw materials factors: >20 meshes milled size and 7-14 meshes original size and 3 speeds of agitator factors: 2620, 1280 and 620 rpm with 4 replications and fixed conditions in both suspending agent: 3% xanthan gum and temperature of solution: 30-40°C.

The total amounts of 119.6 g urea each were divided into 72.1 g urea 1 being fed for clear liquid mixed solution stage (the first stage) and 47.5 g urea 2 being fed for suspended solution stage (the second stage) (**Table 12**). The processes were the addition of 72.1 g urea 1 in the first stage, with the addition of 6.6 g xanthan gum, 9.1 g KCl, 29.7 g MKP and 47.5 g urea 2 in the second stage, simultaneously, into the cylindrical glass bottle containing 55.0 g water mounted to the adjustable speeds.

The suspension fertilizers from each treatment were evaluated for physical properties, dissolving time (the time for completely dissolved urea 1 and xanthan gum in the first and the second stage, respectively). The dissolving time for urea 1 and xanthan were detected by counting the time from urea 1 and xanthan yielding to its

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completely dissolved and viscous solution, respectively. All of the raw data were evaluated for analysis of variance in R program.

Table 12 Particle sizes, speeds of agitator and quantity of raw materials that were equal in each treatment for processing of 25-7-7 analysis grades of suspension fertilizer

Treatments										
no.	Particle size of raw materials	Speeds of agitator (rpm)			Quantity of raw materials (gram)					Total
					The first stage		The second stage			
		2620 (S1)	1280 (S2)	620 (S3)	water	urea 1	KCl	MKP	urea 2	
Tr1	>20 mesh (M1)	M1S1			55.0	72.1	9.1	29.7	47.5	220
Tr2	>20 mesh (M1)		M1S2		55.0	72.1	9.1	29.7	47.5	220
Tr3	>20 mesh (M1)			M1S3	55.0	72.1	9.1	29.7	47.5	220
Tr4	Original (M2)	M2S1			55.0	72.1	9.1	29.7	47.5	220
Tr5	Original (M2)		M2S2		55.0	72.1	9.1	29.7	47.5	220
Tr6	Original (M2)			M2S3	55.0	72.1	9.1	29.7	47.5	220

Note: all of treatments were treated by 6.6 g xathan gum and temperature of solution: 30-40°C, urea (46-0-0), KCl (0-0-60), MKP (0-52-34)

Experiment 2: Effects of the temperature of solution and the suspending agent on production method of 25-7-7 analysis grade of suspension fertilizer

The experimental design was a 2x3 factorial experiment in CRD. They were 2 temperatures of solution factors: 30-40°C and 50-60°C and 3 concentrations of suspending agent factors: 2.5, 3 and 5% xanthan gum with 4 replications. In fixed conditions, >20 meshes milled size of raw materials and 1280 rpm speed of agitator were used in the first stage and 2620 rpm for the second stage.

Treatment 1 preparation was the addition of 72.1 g urea 1 in the first stage using 1280 rpm speed, followed by the addition of 5.5 g xanthan gum, 9.1 g KCl, 29.7 g MKP, and 47.5 g urea 2 in the second stage, simultaneously, into the **bottle**

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containing 56.1 g water mounted to the adjustable speeds of agitator using 2620 rpm speed. The quantity of water in Treatment 2 to 6 were varied with concentration of xanthan gum used (**Table 13**).

The suspension fertilizers from each treatment were evaluated for physical properties using various equipments and calculations as follows: 1) the pH using portable pH meter, Checker® from USA, 2) specific gravity using specific gravity hydrometer, 3) stability using calculation of amounts of clear liquid (supernatant) on the top of the suspension fertilizer in a graduate cylinder after standing undisturbed for 24 hours (Browder and Ulmer, 1971), 4) pour-ability using calculation of amounts of the poured products and the remained products which were poured from the bottle after standing undisturbed for 24 hours (CIPAC, 2009 a; Salladay and Kachelman, 1986), 5) viscosity using detecting with Brookfield digital viscometer (CIPAC, 2009 c; Davenport *et. al*., 1978), and 6) salting out using calculation of amounts of retained crystals of the product on the 20 mesh standard test sieve (CIPAC, 2009 b, 2009; Byrd and Scott, 1979). All of the raw data were evaluated for analysis of variance in R program.

Table 13 Temperatures of solution, suspending agents and quantity of solid raw materials for processing of 25-7-7 analysis grades of suspension fertilizer

Treatments											
No.	Temperatures of solution	Suspending agents (% Xanthan gum)			Quantity of solid raw materials (gram)						Total
					The first stage with 1280 rpm		The second stage with 2620 rpm				
		2.5 (G1)	3 (G2)	5 (G3)	Water	urea 1	gum	KCl	MKP	urea 2	
Tr1	30-40°C (T1)	T1G1			56.1	72.1	5.5	9.1	29.7	47.5	220
Tr2	30-40°C (T1)		T1G2		55.0	72.1	6.6	9.1	29.7	47.5	220
Tr3	30-40°C (T1)			T1G3	50.6	72.1	11.0	9.1	29.7	47.5	220
Tr4	50-60°C (T2)	T2G1			56.1	72.1	5.5	9.1	29.7	47.5	220
Tr5	50-60°C (T2)		T2G2		55.0	72.1	6.6	9.1	29.7	47.5	220
Tr6	50-60°C (T2)			T2G3	50.6	72.1	11.0	9.1	29.7	47.5	220

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Experiment 3: Effects of stored periods on physical properties of 25-7-7 analysis grade of suspension fertilizer through Luxen's method

Luxen's method which was significantly effective to the suspension fertilizer production method was consisted of 4 factors as following: 1. The milled raw materials in particle size of >20 meshes, 2. The speeds of agitator: 1280 rpm for clear liquid mixed solution stage and 2620 rpm for suspended solution stage, 3. The temperature of solution in 30-40°C, and 4. Suspending agent: 2.5% xanthan gum.

25-7-7 analysis grade of suspension fertilizers were processed by Luxen's method. The experiment was designed in CRD with 6 stored periods' factor: 0, 7, 15, 30, 90, and 180 days, total of 6 treatments with 4 replicates. The process was to add 72.1 g of urea 1 in clear liquid mixed solution stage with 1280 rpm speed, simultaneously, 5.5 g of xanthan gum, 9.1 g of KCl, 29.7 g of MKP, and 47.5 g of urea 2 in suspended solution stage with 2620 rpm speed, respectively, into the bottle which was mounted to the adjustable speeds of mixer and presented 56.1 g of water (**Table 14**). The suspensions were agitated for homogenize.

The received 25-7-7 suspensions were stored undisturbed in the variously stored periods at normal room temperature.

The suspension fertilizers from each treatment were evaluated for physical properties using various equipments and calculations as follows: 1) the pH using portable pH meter, Checker® from USA, 2) specific gravity using specific gravity hydrometer, 3) stability using calculation of amounts of clear liquid (supernatant) on the top of the suspension fertilizer in a graduate cylinder after standing undisturbed for 24 hours (Browder and Ulmer, 1971), 4) pour-ability using calculation of amounts of the poured products and the remained products which were poured from the bottle after standing undisturbed for 24 hours (CIPAC, 2009a; Salladay and Kachelman, 1986), 5) viscosity using detecting with Brookfield digital viscometer (CIPAC, 2009 c; Davenport *et. al.*, 1978), and 6) salting out using calculation of amounts of retained

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crystals of the product on the 20 mesh standard test sieve (CIPAC, 2009b; Byrd and Scott, 1979). All of the raw data were evaluated for analysis of variance in R program.

Table 14 Treatments, quantity of raw materials and stored periods for 25-7-7 analysis grade of suspension fertilizer

Treatments								
No.	Quantity of raw materials (g)							Stored periods (d)
	water	U 1	gum	KCl	MKP	U 2	total	
Tr_1	56.1	72.1	5.5	9.1	29.7	47.5	220	0
Tr_2	56.1	72.1	5.5	9.1	29.7	47.5	220	7
Tr_3	56.1	72.1	5.5	9.1	29.7	47.5	220	15
Tr_4	56.1	72.1	5.5	9.1	29.7	47.5	220	30
Tr_5	56.1	72.1	5.5	9.1	29.7	47.5	220	90
Tr_6	56.1	72.1	5.5	9.1	29.7	47.5	220	180

Note: U= >20 meshes milled urea, gum = xanthan gum, KCl = potassium chloride, MKP = mono potassium phosphate

Experiment 4: Effects of quantity and kinds of solid raw materials in Luxen's Method on various suspension fertilizer grades

The experiment design was 4x6 factorial experiment in CRD with 4 replications. There were 4 stored period factors: 0, 30, 90, and 180 days, and 6 analysis grades of suspension fertilizer factor that were processed by Luxen's method: high N ratio of 25-7-7 and 20-10-10, high P_2O_5 ratio of 12-24-12 and 7-21-21, high K_2O ratio of 13-13-21, and in equal ratio of 15-15-15 (**Table 15**; **15.1**). The total amounts of urea in each analysis grade of suspension fertilizer were divided into 2 portions, the one (urea 1) being fed in clear liquid mixed solution stage (the first stage) with 1280 rpm speed, the other (urea 2) being fed in suspended solution stage (the second stage) with 2620 rpm speed. **Table 9** showed the preliminary experiment

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resulted in physical properties of solid raw materials, xanthan gums and saturated solution.

The process of 25-7-7 suspension fertilizer was to add 72.1 g urea 1 in clear liquid mixed solution stage (the first stage), simultaneously, 5.5 g xanthan gum, 9.1 g KCl, 29.7 g MKP and 47.5 g urea 2 in suspended solution stage (the second stage), respectively, into the bottle which was mounted to the adjustable speeds of mixer and presented 56.1 g water (**Table 15; 15.1**). The suspensions were agitated for homogenize. At last 25-7-7 suspension fertilizer was received. The remaining suspension fertilizer grades were the same process with their components in **Table 15**; **15.1**.

The suspension fertilizers from each treatment were evaluated for chemical and physical properties using various equipments and calculations as follows: 1) analyzing chemical property, after the each treatment had been stored at 180 d, the suspension from 4 replications were sampled for analyzing chemical property: N, P_2O_5 and K_2O (AOAC International, 2000), 2) the pH using portable pH meter, Checker®from USA, 3) specific gravity using specific gravity hydrometer, 4) stability using calculation of amounts of clear liquid (supernatant) on the top of the suspension fertilizer in a graduate cylinder after standing undisturbed for 24 hours (Browder and Ulmer, 1971), 5) pour-ability using calculation of amounts of the poured products and the remained products which were poured from the bottle after standing undisturbed for 24 hours (CIPAC, 2009a; Salladay and Kachelman, 1986), 6) viscosity using detecting with Brookfield digital viscometer (CIPAC, 2009c; Davenport *et. al*., 1978), and 7) salting out using calculation of amounts of retained crystals of the product on the 20 mesh standard test sieve (CIPAC, 2009b; Byrd and Scott, 1979). All of the raw data were evaluated for analysis of variance in R program.

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Table 15 Analysis grades of suspension fertilizer and theirs components

Suspension fertilizer grades	Quantity of raw materials							Total
	The first stage[1/]				The second stage[2/]			
	water	urea 1	gum	MAP	KCl	MKP	urea 2	
25-7-7 (Gr1)	56.1	72.1	5.5[3/]	-	9.1	29.7	47.5	220.0
20-10-10 (Gr2)	62.8	75.0	6.6[4/]	-	12.7	42.3	20.6	220.0
12-24-12 (Gr3)	57.3	45.9	6.6[4/]	44	15.4	50.8	-	220.0
13-13-21 (Gr4)	52.6	62.3	4.4[4/]	-	45.7	55.0	-	220.0
7-21-21 (Gr5)	65.5	33.5	5.5[4/]	-	26.7	88.8	-	220.0
15-15-15 (Gr6)	58.1	40.0	7.7[4/]	-	19.1	63.4	31.7	220.0

Note: [1/]= with 1280 rpm speed of agitator, [2/]= with 2620 rpm speed of agitator, [3/]= as the experiment 2, [4/]= as the preliminary experiment results in ranging 2-3.5% gum

Table 15.1 Analysis grades of suspension fertilizer were stored at various periods

Suspension fertilizer grades	Stored periods (day)			
	0 (D0)	30 (D30)	90 (D90)	180 (D180)
25-7-7 (Gr1)	Tr1 (Gr1D0)	Tr2 (Gr1D30)	Tr3 (Gr1D90)	Tr4 (Gr1D180)
20-10-10 (Gr2)	Tr5 (Gr2D0)	Tr6 (Gr2D30)	Tr7 (Gr2D90)	Tr8 (Gr2D180)
12-24-12 (Gr3)	Tr9 (Gr3D0)	Tr10 (Gr3D30)	Tr11 (Gr3D90)	Tr12 (Gr3D180)
13-13-21 (Gr4)	Tr13 (Gr4D0)	Tr14 (Gr4D30)	Tr15 (Gr4D90)	Tr16 (Gr4D180)
7-21-21 (Gr5)	Tr17 (Gr5D0)	Tr18 (Gr5D30)	Tr19 (Gr5D90)	Tr20 (Gr5D180)
15-15-15 (Gr6)	Tr21 (Gr6D0)	Tr22 (Gr6D30)	Tr23 (Gr6D90)	Tr24 (Gr6D180)

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Experiment 5: Effects of 25-7-7 analysis grade of suspension fertilizer in drip fertigation system on plant growth, yield and nutrient concentrations of Chinese kale (*Brassica oleracea* var. *alboglabra*) in Pot

The comparative study of the effects of 25-7-7 analysis grade of suspension fertilizer and 25-7-7 granule fertilizer on growth of Chinese kale was conducted in Complete Randomize Design with 5 treatments and 5 replications in the nursery (**Table 16**). The 25-7-7 analysis grades of suspension fertilizers which were produced by Luxen's Method.

There were 25 black plastic pots in 8" diameter contained 3 kilograms of soil base media (soil: coconut coir dust: burnt rice husk: rice husk =2:2:1:1 v/v) with one seedling of Chinese kale.

Tr_1 was non-fertilizer application by both the granule and the suspension fertilizers. Tr_2 was applied under broadcasting the 25-7-7 analysis grades of granule fertilizers at the rate of 353 mg/pot/event, total of 5 events. The broadcasting times were 7, 14, 21, 28 and 35 days after transplanting (DAT). Tr_3, Tr_4 and Tr_5 were applied under drip fertigation system by fertigating 25-7-7 analysis grades of suspension fertilizers at the rate of 49, 98 and 196 mg/pot/event, respectively, total of 18 events, every other day, as **Table 16**.

Watering 200 ml was twice a day for Tr_1 and Tr_2, dripping Tr_3, Tr_4 and Tr_5 with 200 ml of the solution in concentration of 0.0245%, 0.049% and 0.098% of 25-7-7 suspension fertilizer for 20 minutes, those concentrations were equivalent to the rate of 49, 98 and 196 mg/pot/event, respectively, as mentioned events above, and dripping with 200 ml of blank water instead of the fertilizer solutions for twice a day.

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Table 16 Types of fertilizers, application rates, frequency and total amounts of fertilizer application for each treatment of experiment 5

Treatments	Types of fertilizer, application rates and frequency					
	25-7-7 of granule by broadcasting			25-7-7 of suspension fertilizer by fertigation		
	Rate (mg/pot /event)	Events (DAT)[1]	Total (mg/pot)	Rate (mg/pot/ event)	No. of application[1] (times)	Total (mg/pot)
Tr_1 (control)	-	-	-	-	-	-
Tr_2	353	7, 14, 21, 28, 35	1764	-	-	-
Tr_3				49	18	882
Tr_4				98	18	1764
Tr_5				196	18	3528

Note: [1]= day after transplanting

Data collection

Physical and chemical properties of soil base media after applications:

1. pH was tested by electrometry method with pH meter (Sartorius, PB20) (Soil Chemical Research Group, 2001).

2. Electrical conductivity (ECe) was tested by electrical conductivity meter (Hana, HI 8733) (Soil Chemical Research Group, 2001).

3. Organic matter (OM) was analyzed by wet oxidation (Tassanee and Chongrax, 1999).

4. Available phosphorous was analyzed by Bray II and analyze phosphorous concentration by colorimetry with spectrophotometer (Milton Roy, Spectonic Genesys 5, USA) (Soil Chemical Research Group, 2001).

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5. Exchangeable potassium, calcium and magnesium were analyzed by extracted with ammonium acetate and analyze potassium, calcium and magnesium concentration by atomic absorption spectrophotometer (Analytic Jena, vario 6, Jena, Germany) (Soil Chemical Research Group, 2001).

Growth of Chinese kale

1. Plant height at 14, 21, 28, 35 and 45 DAT by measure between the soil surface in black plastic pot to the highest of Chinese kale leaf with a scale

2. Leaf greenness color in SPAD unit at harvest stage (Minolta Chlorophyll Meter: SPAD-502, Japan)

Yield of Chinese kale

1. Total plant fresh weight of Chinese kale leaf (g/plant)

2. Total plant dried weight of Chinese kale leaf (g/plant)

Nutrient concentrations in Chinese kale leaf

1. Nitrogen concentration: analyze nitrogen concentration by combustion, the Chinese kale leaf which were dried, milled and sieved were wrapped with a nitrogen less foils (LECO) and then were burn in protein / nitrogen determinator (LECO, FP-528, Miami, USA). To be obtained the total % nitrogen.

2. Digestion of the Chinese kale leaf with sulphuric acid (H_2SO_4) conc.

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3. Phosphorus concentration: analyze phosphorous concentration in the Chinese kale leaf by colorimetric method (Tassanee and Chongrax, 1999) (Appendix), the digested samples were added solution of ammonium molybdate (5%) and ammonium metavanadate (0.25%). The solutions were detected with wave length in Spectrophotometer (Milton Roy series Spectonic Genesys 5, USA)

4. Potassium concentration: analyze potassium concentration in the Chinese kale leaf by Atomic Absorption Spectrophotometry (Tassanee and Chongrax, 1999) (Appendix), the digested samples were detected with wave length in Atomic Absorption Spectrophotometer (Analytic Jena, vario 6, Jena, Germany)

The experimental data were statistically evaluated for Analysis of Variance (ANOVA) in R- program.

To evaluate the fertilizer cost between suspension fertilizer and granule fertilizer

During 2012-2014, the rate of use, suitable timing, price of granule fertilizer and recommendations for Chinese kale were supported by Department of Agriculture, manufacturers and wholesalers. At the same time, the suspension fertilizer recommendations were supported by Captain Fertilizer Company. All of data were evaluated for fertilizer cost.

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RESULTS AND DISCUSSION

Experiment 1

The particle sizes were found to be significantly different in dissolving time for urea 1 **(Table 17)**. The solutions processed by > 20 meshes milled raw materials were spent less dissolving time than original size (1.136 and 5.574 min). At the same time, the speeds of agitator significantly affected on dissolving time for urea 1. The 2620 rpm speed of agitator gave, on average, the shortest dissolving time of 2.491 min, and the 620 rpm speed of agitator gave the longest dissolving time of 3.99 min. There was an interaction between particle sizes and speeds of agitator on dissolving time for urea 1. The solutions that were processed using original size of raw material with 1820 or 620 rpm speeds of agitator took the longest dissolving time, 6.247-6.317 min, while the use of > 20 meshes of milled raw materials with 2620 or 1820 rpm speeds of agitator consumed the shortest dissolving time: 0.825-0.922 min.

The milled raw materials and high speeds of agitator caused shorter dissolving time for the raw materials being completely dissolved. This could be attributed to the smaller particle size of milled raw materials of >20 meshes comparing to the larger particle size of 7-14 mesh of original size. This size of milled raw materials had more surface areas in the solution. In fact, the surface areas did not affect the amounts of urea 1 in dissolution, but they did affect the higher rate of dissolution of urea 1. The high~~er~~ speeds of agitator brought fresh water into contact with urea 1 and so permitted a faster rate of dissolution. The results were similar to that of Chang (2004) in that the factors affecting the rate of dissolution were surface area, rate of stirring and temperature of solution.

The process which was treated by >20 meshes of milled raw materials with 1820 rpm speeds of agitator in the first stage was appropriate.

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In this experiment, urea was used for the first time in the process of solubility investigation because of its higher solubility than remaining raw materials, MKP and KCl (**Table 9**).

The conventional process, the UAN (urea ammonium nitrate solution) and APP (ammonium polyphosphate) have been used in base solution. KCl would be fed into the solution with clay as suspending agent in order to receiving a suspended KCl.

Table 17 Effects of speeds of agitator and particle size of solid raw materials on the dissolving time for urea 1 being dissolved completely

Speeds of agitator (rpm)	Particle size		S-average
	M1 (>20 meshes)	M2 (original: 7-14 meshes)	
	Dissolving time for urea 1 (minute)		
S1 (2620)	0.825 d	4.157 b	2.491 Z
S2 (1820)	0.922 d	6.247 a	3.585 Y
S3 (620)	1.662 c	6.317 a	3.990 X
M-average	1.136 B	5.574 A	3.355
F-Test	M	S	MS
	*	*	*
C.V. (%)	9.47		

Note: Means in a column and a row followed by the same letter are not significantly different, * significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

From Table 18, the particle sizes of raw materials were non-significantly different in dissolving time for completely dissolving xanthan gum. Both particle sizes were found to take an average of 3.393-3.409 min in dissolving time for xanthan gum. At the same time, the speeds of agitator gave significantly different in dissolving time for xanthan gum. The shortest average dissolving time of 1.389 min was found

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when using 2620 rpm speed of agitator and 6.676 min dissolving time when using 620 rpm speed of agitator, the longest average dissolving time. The interaction between particle sizes and speeds of agitator were non-significantly different in dissolving time for xanthan gum. The suspensions processed by >20 meshes milled raw materials as well as by the original size using the 2620 rpm speeds of agitator took 1.380-1.398 min dissolving time of xanthan gum. While those suspensions processed by the same raw materials with 620 rpm speeds of agitator took 6.672-6.680 min dissolving time of xanthan gum.

The results showed that the use of higher speeds of agitator took shorter dissolving time for xanthan gum being completely dissolved. This could be described that the powder state of xanthan gum had more surface areas and good solubility which formed in 3 dimension networks in the solution. Some of them were occurred in lump and more amounts of forces (high speeds of agitator) would be required to destroy them and to bring fresh water into contact with them.

It could be concluded that the process treated by >20 meshes of milled raw materials using 2620 rpm speeds of agitator in the second stage was appropriate.

For further operation in the experiment 2, the medium speed (1280 rpm) would be used in the first stage and higher speed (2620 rpm) of agitator in the second stage under using >20 meshes of milled raw materials.

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Table 18 Effects of speeds of agitator and particle size of solid raw materials on the dissolving time for xanthan gum being dissolved completely

Speeds of agitator (rpm)	Particle size		S-average
	M1 (>20 meshes)	M2 (original: 7-14 meshes)	
	Dissolving time for xanthan gum (minute)		
S1 (2620)	1.398	1.380	1.389 Z
S2 (1820)	2.150	2.125	2.138 Y
S3 (620)	6.680	6.672	6.676 X
M-average	3.409	3.393	
F-Test	M	S	MS
	ns	*	ns
C.V. (%)		1.61	

Note: Means in a column and a row followed by the same letter are not significantly different, * significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

Experiment 2

The results showed that all of 6 treatments were of non-caking, homogenized, suspended fertilizer types that the suspensions were suspended by xanthan gum. Their components consisted of needle crystals of urea 1, suspended urea 2, suspended KCl, suspended MKP and suspended liquid (**Figure 33** and **34**).

It was revealed that 72.1 g urea 1 was completely dissolved in 61.6 g water treated by the desired temperatures (30-40°C and 50-60°C) in the first stage. It resulted in getting the saturated solutions. The desired suspending agent, xanthan gums (2.5, 3 and 5%) were fed into saturated solutions and became saturated suspension solutions that affected on viscous solutions [3 dimension networks of xanthan gum solution (Figure 35)] with suspension properties (Wolf *et. al.*, 1985).

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The remaining 9.1 g KCl, 29.7 g MKP and 47.5 g urea 2 were fed into the saturated suspension solutions in the second stage, simultaneously. All of them could be dissolved a little amounts, and the large number of remaining solid particles were not dissolved which would be attracted to xanthan gum by van der Waals force (**Figure 35**) and formed in the saturated suspension solutions. At the same time, the saturated suspension solutions were become to the super saturated suspension solutions which would have crystallization for crystals of urea 1 molecular formation in that solution [the crystals of urea 1 which were molecular crystals were formed by van der Waals force: Cohesive force (DCFSC, 2012)]. According to the super saturated suspension solutions which had suspension property, urea 1 molecules and the crystals of urea 1 were surrounded by xanthan gum (urea 1 molecules and the crystals of urea 1 were also attracted to xanthan gum by van der Waals force in 3 dimension networks of xanthan gum solution, **Figure 35**). The formation of the gelatinous molecules of urea 1 in long crystals (large crystal growth) was limited which affected the formation of smaller crystals (needle) of urea 1 in the suspended solution instead. The suspended solutions were homogenized and suspended with no sediment and no caking (**Figure 33**). This pathway was explained by Mier's theory (Khanam, 2007), van der Waals force and suspension property of Xanthan gum. The result of this investigation was in agreement with the previous researches in that significant suspending agent was found confirming that the suspension fertilizers should consist of following suspending agents, attapulgite, sepiolite, sodium bentonite and polysaccharides (Wolf *et. al*., 1985; Salladay *et. al*., 1984; Richard and Charles, 1976; Colegrove, 1984; Fraley and Rogers, 1997; Benjamin and Kohn, 1962).

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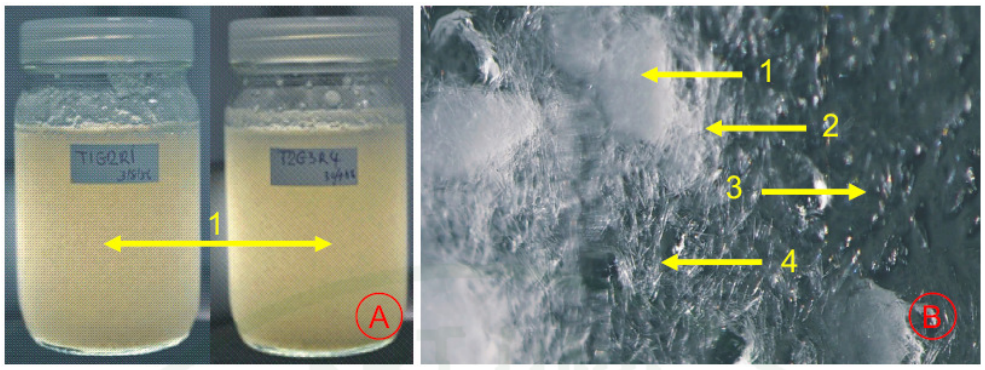

Figure 33 The suspension fertilizers with 1 = non-caking, homogenize and suspended (A), the magnified picture of the components of 25-7-7 suspension (B): 1=suspended urea 2, 2=suspended KCl, 3=suspended liquid and 4= needle crystals of urea 1

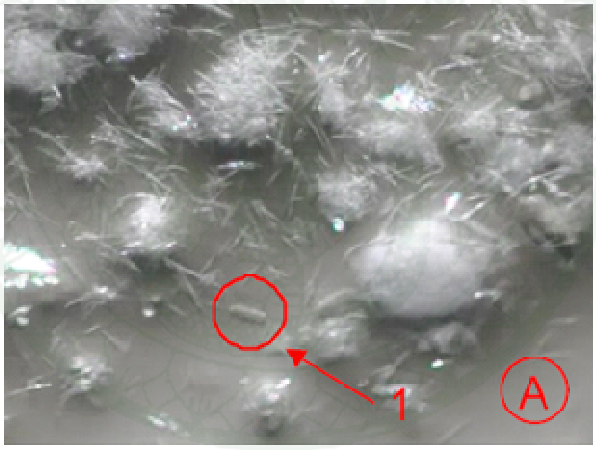

Figure 34 The magnified picture of the components of 25-7-7 suspension (A) 1=suspended MKP

Structure of suspension fertilizer

The structure of 25-7-7 analysis grade of suspension fertilizer (Figure 35) was found in this research. They were consisted of suspended water, xanthan gum, needle crystals of urea 1 and non-dissolved raw materials (urea 2, MKP and KCl). All of the materials were linked together with various attractive forces as the proposed structure

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in **Figure 35**. After the feeding of Xanthan gum into the urea 1 solution in the first stage, the linkage with water molecules were formed in the solution with hydrogen bond. The formation of 3

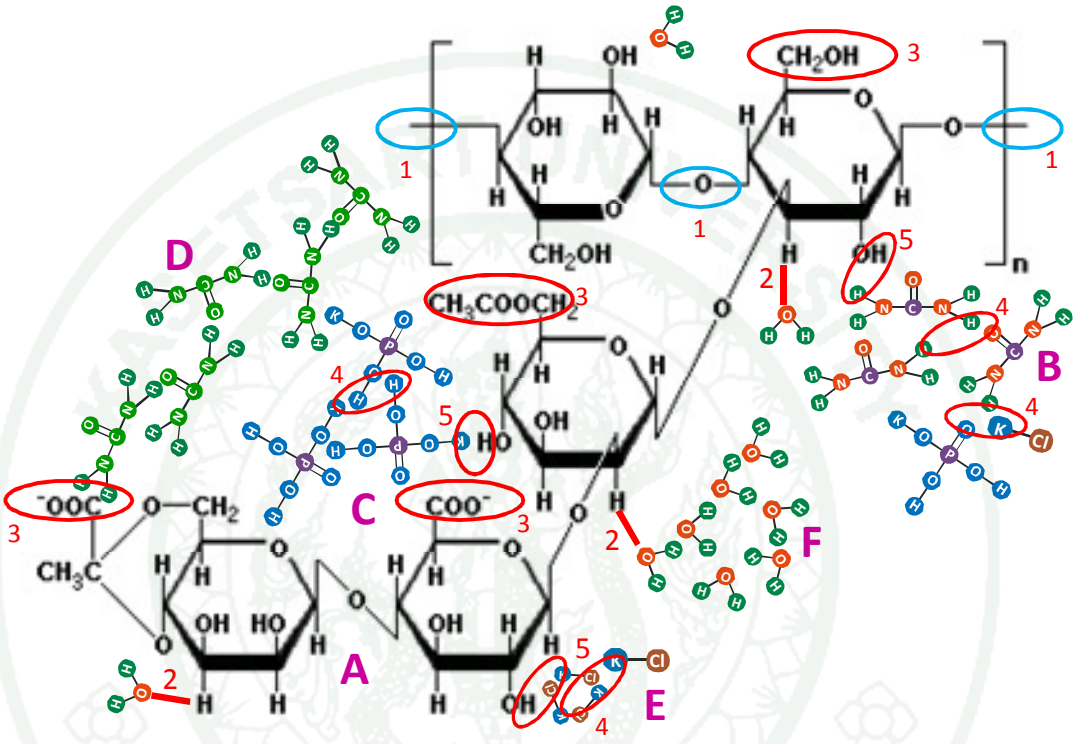

Figure 35 Structure of suspension fertilizer, linkage among xanthan gum, H_2O, non-dissolved raw materials: urea 2, KH_2PO_4 and KCl and needle crystals of urea 1, A = xanthan gum, B = urea 2, C = KH_2PO_4, D = needle crystals of urea1, E = KCl, F = H_2O, 1 = covalent bond, van der Waals force: 2 = hydrogen bond, 3 = carboxyl group, 4 = intermolecular force, 5 = hydroxyl group

Source: modified from Anil (2012)

dimension networks of xanthan gum solution occurred with 5 types of attraction forces. At the finished process, the bond formations were going to occur, simultaneously, each xanthan gum portion could be previously cross- linked together (at C1-C4 of β-D-glucose 2 molecules) in 3 positions in each by covalent bond for big agglomerate (Anil. 2012), water molecules could be attracted to xanthan gum by

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hydrogen bonds for formation of 3 dimension networks of xanthan gum solution which were deranged (entanglement), 4 carboxyl groups on xanthan gum could be attracted by each xanthan gum and some non-dissolved raw materials, the non-dissolved raw materials could be attracted among them by Intermolecular force, many hydroxyl groups on xanthan gum could be attracted by some non-dissolved raw materials (NQF-AGRO, 2001; Aimtrakarn*et al*., 2011). All of these attraction forces, van der Waals force with weakly cross-linked forces, had affected on viscosity and suspended solution suspended the non-dissolved raw materials for non-sedimentation.

pH

From **Table 19**, the temperatures of solution factor gave significantly different in pH. The suspension fertilizers treated by temperature of solution 30-40°C showed an average pH of 5.55 which was lower than that of temperature 50-60°C with the average pH 5.68.

At the same time, the suspending agent factor gave non-significantly different in pH. The suspension fertilizers treated by various concentrations of xanthan gum (2.5-5%) gave average pH of 5.53-5.67.

Furthermore, the interaction between suspending agent and temperatures of solution were found to be non- significantly different in pH. The suspension fertilizers were treated by both the temperatures (30-40°C and 50-60°C) and various concentrations of xanthan gum (2.5-5%) gave the pH 5.47-5.77.

It was found that high temperature of the solution (50-60°C) had resulted in high pH of the solution. These could be described that higher temperatures could dissolve as many particles of urea 2 and KCl, causing high pH in the solution (**Table 9**). The addition of large amounts of suspending agents (xanthan gum) had resulted in low pH of the solutions. These could attribute to acidic property of xanthan gums which gave the acid in the solution (**Table 9**).

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Table 19 Effects of suspending agent and temperatures of solution on pH of 25-7-7 analysis grade of suspension fertilizer

Suspending agent (% xanthan gum)	Temperatures (°C)		G-average
	T1 (30-40)	T2 (50-60)	
	pH		
G1 (2.5)	5.57	5.77	5.67
G2 (3.0)	5.62	5.67	5.65
G3 (5.0)	5.47	5.60	5.53
T-average	5.55 B	5.68 A	5.61
F-Test	T	G	TG
	*	ns	ns
C.V. (%)		1.95	

Note: Means in a column and a row followed by the same letter are not significantly different, * significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

In the new suspension fertilizer production method, its high pH of the products was not as high as the pH of 7.2 of the 25-7-7 analysis grade of suspension fertilizer imported by Captain Fertilizer Co., Ltd., that evaluated by the Department of agriculture (Captain Fertilizers, 2012). Previous research report (Kendrick, Jr .1974) found also that the pH of suspension fertilizers higher than pH 5.9 would affect on more crystals of DAP and the Lower pH of 5.9 would result in more and more MAP. Miller (1962) found that the proper pH of appropriated suspension fertilizers varied from 7.5 to 8 and the pH higher than 8 would affect on decreasing solubility of nutrients and tended to salting out. It was found that the new production method had no chemical reaction of solid raw materials in process as that in the conventional method, but it involved in solubility of raw materials (in case of consistence of non-dissolved raw materials in the suspensions which could not give Hydroxyl ion: OH^- or Hydrogen ion, H^+ in the suspensions) and the property of suspending agent: xanthan

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gum. The range of pH of the products of 5.47 to 5.77 could be compatible to other agricultural chemicals.

Specific gravity (SG)

From **Table 20**, the SGs of all 6 treatments showed non-significantly different of 1.195-1.243. This illustrated that both temperatures of solution and concentrations of suspending agent (xanthan gum) did not affect on specific gravity of the solutions because there was no chemical reaction of the solid raw materials in the process. In the first stage, only 32.7% of urea 1 dissolved completely. The process had affected less specific gravity of the solution than that of conventional method which reaction product between H_3PO_4 and NH_3 and gave higher specific gravity. This was because of the suspension consisted of N and P_2O_5. So 25-7-7 analysis grade of suspension fertilizers in this research had specific gravities 1.195-1.243. The SG of the 25-7-7 analysis grade of suspension fertilizer processed by ammoniation to H_3PO_4 and imported by Captain Fertilizer Co., Ltd. was found to be 1.29 analyzed by Department of Agriculture (Captain Fertilizers, 2012).

The measurement of specific gravity pointed out many things about the relative compositions of fluid fertilizers when correlated with other data of particular solution or suspension. That parameter is commonly processed at the temperature of 25°C and is useful in adjusting calibrated application equipment to obtain accurate application rates for the particular fluid fertilizers (Wolf *et. al.*, 1985).

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Table 20 Effects of suspending agent and temperatures of solution on specific gravity of 25-7-7 analysis grade of suspension fertilizer

Suspending agent (% xanthan gum)	Temperatures (°C)		G-average
	T1 (30-40)	T2 (50-60)	
	Specific gravity		
G1 (2.5)	1.229	1.243	1.236
G2 (3.0)	1.233	1.194	1.214
G3 (5.0)	1.201	1.211	1.206
T-average	1.221	1.216	1.218
F-Test	T	G	TG
	ns	ns	ns
C.V. (%)		2.18	

Note: Means in a column and a row followed by the same letter are not significantly different, * significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

Viscosities

From **Table 21**, temperatures of solution gave significantly different in its average viscosity. The suspensions treated by the temperature of 30-40°C of solution gave the average viscosity of 5143 mPa.s and higher than that of suspensions treated by the temperature of 50-60°C of solution with the average viscosity of 3309 mPa.s. The results could be interpreted that higher temperature enhanced dissolution of KCl, MKP and urea 2 in the second stage which was related to the research of Eibner *et al.,* (1985). The quantity of the suspended solid raw materials was found to be fewer amounts in the second stage which affected on low density and low viscosity of the suspended solutions (**Table 21**). The result in low viscosity of the suspension had to be detected by Brookfield Viscometer exactly. So, the high temperatures of solution affected on low viscosity of the suspension (**Table 21**).

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At the same time, the effect of suspending agent on viscosity showed significantly different. Higher percentage of suspending agent (xanthan gum) of 5, 3 and 2.5% had affected on high average viscosity of 6997, 4035, and 1646 mPa.s of the suspensions, respectively. The results could be interpreted that xanthan gum was suspending agent which affected on viscosity of the suspension and enhancing suspension property (Wolf *et. al*., 1985; Salladay *et. al*., 1984; Colegrove, 1984). **Figure 35** showed that high xanthan gum percentage had affected on high entanglement density of xanthan gum polymer (high 3 dimension network) in the suspension that resulted in high viscosity (NQF-AGRO, 2001).

Furthermore, the interaction between temperatures of solution and suspending agent showed significantly different in viscosity. The suspensions treated by temperature of 30-40°C or 50-60°C with 2.5% xanthan gum gave low viscosity of 1633-1659 mPa.s. While the temperature of 30-40°C with 5% xanthan gum gave high viscosity of 8657 mPa.s (**Table 21**, **Figure 36**).

The structure of suspension fertilizer consisted of xanthan gum, water molecule, urea, MKP and KCl which linked to each other by van der Waals force for high entanglement density (**Figure 36**). There were 5 types of attractive forces; 1 = covalent bond, 2 = hydrogen bond, 3 = carboxyl group, 4 = intermolecular force and 5 = hydroxyl group, for one unit of xanthan gum. The high entanglement density depended on high concentration of xanthan gum in suspension. Therefore, the measurement of viscosity could be made using higher shear rates more than that in the Brookfield viscometer which affected on high viscosity since all attractive forces was destroyed by higher shear rates.

So the suspensions treated by temperature of 30-40°C or 50-60°C with 2.5% xanthan gum gave low viscosity of 1633-1659 mPa.s and the suspensions treated by temperature of 50-60°C with 3% xanthan gum gave viscosity of 2930 mPa.s and considered to be appropriate treatments because the optimum viscosities were 1633-2930 mPa.s. The results are in line with the research of Salladay and Kachelman

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(1986) who found that viscosity depends on analysis grade of suspension fertilizers and the amount of suspending agent.

Table 21 Effects of suspending agent and temperatures of solution on viscosity of 25-7-7 analysis grade of suspension fertilizer

Suspending agent (% xanthan gum)	Temperatures (°C)		G-average
	T1 (30-40)	T2 (50-60)	
	Viscosity[1/] (mPa.s)		
G1 (2.5)	1633 d	1659 d	1646 Z
G2 (3.0)	5139 b	2930 c	4035 Y
G3 (5.0)	8657 a	5337 b	6997 X
T-average	5143 A	3309 B	4226
F-Test	T	G	TG
	*	*	*
C.V. (%)		13.8	

Note: [1/] by Brook field viscometer, spindle # 3 and 4, 30 rpm, time 2 minute
Means in a column and a row followed by the same letter are not significantly different, * significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

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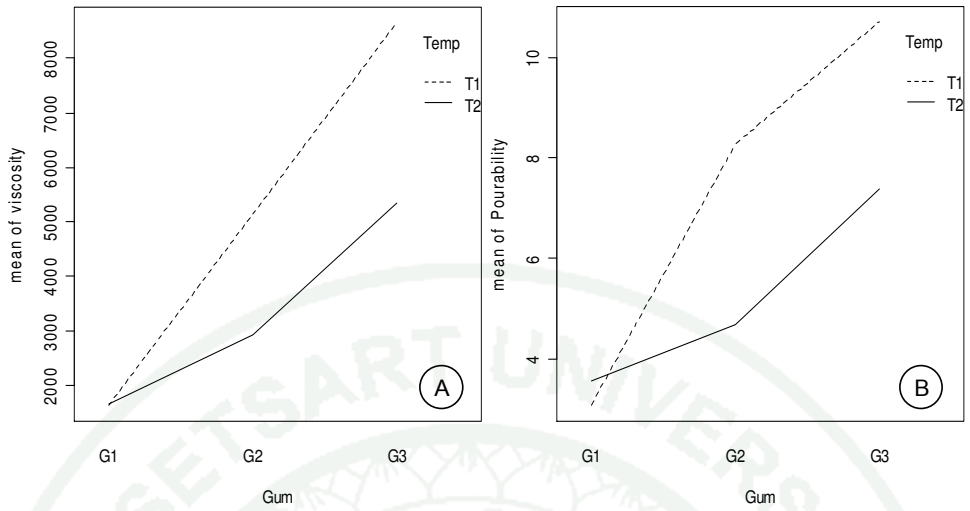

Figure 36 Plotting of interaction between temperature of solution and gum on viscosity (A) and pour-ability (B)

Stability

All of 6 treatments gave 100% apparent solid stability at the initial time, which showed non-significantly different (**Table 22**). These could mean that there was no volume of clear liquid on the top of the suspension (supernatant) in spite of all of treatments treated by various amounts of xanthan gum suspending agent which would affect on the difference in suspension property in the suspensions (as described above in structure of suspension fertilizer). The determination of the apparent solid percentage would be evaluated after the storage of finished products for various time period of: 7, 15, 30, 90 and 180 d (Browder and Ulmer, 1971) since bonding formation was taken more time. The present work was conducted after the products were allowed to stand undisturbed for 24 hours. So the percentage of apparent solids of all treatments gave the same result as 100% apparent solids at the initial time and showed non-significantly different. Thereby, all of the concentration of suspending agent in this research that gave the same result as 100% apparent solid at the initial time may be sufficient or insufficient concentration for long stored periods.

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All treatments were excellent in stability at the initial time. The results were comparable to the acceptable limits of 100% apparent solid stability which showed excellent stability (Browder and Ulmer, 1971).

Table 22 Effects of suspending agent and temperatures of solution on stability of 25-7-7 analysis grade of suspension fertilizer

Suspending agent (% xanthan gum)	Temperatures (°C)		G-average
	T1 (30-40)	T2 (50-60)	
	Stability (% apparent solid)		
G1 (2.5)	100	100	100
G2 (3.0)	100	100	100
G3 (5.0)	100	100	100
T-average	100	100	100
F-Test	T	G	TG
	ns	ns	ns
C.V. (%)		1.8	

Note: Means in a column and a row followed by the same letter are not significantly different, * significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

Pour-ability

From **Table 23,** the temperatures of solution showed significant difference in pour-ability of suspension. The 30-40°C temperature treatment of solution gave lower pour-ability (7.4% the remaining product) than that of 50-60°C which gave higher pour-ability (5.2% the remaining product).

At the same time, the effect of suspending agent on pour-ability showed significantly different. The increasing percentages of xanthan gum suspending agents

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(2.5, 3 and 5%) tend to decrease the pour-ability and the remaining products in the containers were 3.3, 6.5 and 9.1%, respectively.

Furthermore, the interactions between temperatures of solution and suspending agent showed significantly different in pour-ability. The suspensions treated by 30-40°C temperature with 5% xanthan gave low pour-ability of 10.7% the remaining product. While 30-40°C with 2.5% xanthan, 50-60°C with 2.5% xanthan gum and 50-60°C with 3% xanthan gum gave high pour-ability with 3.0, 3.5, and 4.6% remaining product, respectively (**Table 23**, **Figure 36**).

Table 23 Effects of suspending agent and temperatures of solution on pour-ability of 25-7-7 analysis grade of suspension fertilizer

Suspending agent (% xanthan gum)	Temperatures (°C)		G-average
	T1 (30-40)	T2 (50-60)	
	Pour-ability (% remaining product)		
G1 (2.5)	3.0 c	3.5 c	3.3 Z
G2 (3.0)	8.2 ab	4.6 c	6.5 Y
G3 (5.0)	10.7 a	7.3 b	9.1 X
T-average	7.4 A	5.2 B	6.3
F-Test	T	G	TG
	*	*	*
C.V. (%)		26.3	

Note: Means in a column and a row followed by the same letter are not significantly different, * significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

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From **Table 22 and 23**, it could be realized that decreasing the viscosity of the suspension fertilizer from 8657 to 1633 mPa.s resulted in increasing pour-ability of the fertilizers and could be noted on 10.7 to 3% the remaining products.

It could be concluded that the pour-ability was depended on the viscosity of the suspension. The high concentrations of xanthan gum in the suspensions had resulted in high viscosity causing low pour-ability (high % the remaining products). The present research results were in line with the 24-8-8 grade of suspension fertilizer made from liquid raw materials: 12-38-0, UAN (32%N), KCl, 1% clay, 0.3% H_2SiF_6 that gave a low 300-800 mPa.s viscosity which affected on high pour-ability (0% of the remaining products) (Jones and Stinson, 1983).

The high treated Xanthan gums which were employed in suspension fertilizer effected on high entanglement density of xanthan gum polymer (high 3 dimension network) because of cross linkage between xanthan gum and the components in suspension by more amounts of van der Waals forces (**Figure 35**).

The acceptable limits of pour-ability should not be more than 5% the remaining products (CIPAC, 2009a; Salladay and Kachelman, 1986). So the suspensions treated by 30-40°C temperature with 2.5% xanthan, by 50-60°C temperature with 2.5% xanthan gum and by 50-60°C temperature with 3% xanthan gum gave high pour-ability of 3.0, 3.5, and 4.6% remaining product, respectively and considered to be appropriate controlled factors.

Salting out

All treatments gave salting out of 0% retained crystal on the 20 mesh screen sieve at the initial time. The salting out of 0% retained crystal meant that there were no crystals retained after the use of 20 mesh test sieve screening. .All of treatments could produce appropriate suspensions, and in accordant with that of acceptable limits: maximum 2% retained on a 20 mesh sieve (CIPAC, 2009b; Byrd and Scott, 1979).

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The results could be interpreted that all the treatments treated by 30-40°C and 50-60°C temperature factors had resulted in small crystals of nutrient materials in suspension which was in line with the results of many researches such as of Slack and Walters (1963); Richard and Charles (1976) and Kendrick, Jr (1974). These findings had showed that the temperature of solution of 29, 38, and 70-82°C had resulted in small crystals of nutrient materials in the suspension fertilizers. Furthermore, Johnson and Huber (1991) found that a suspension with sufficient gel strength will support the solids contained in the suspension and prevent them from setting out. So the suitable suspending agent for this research was at least 2.5% xanthan gum for the suspensions which gave 0% retained crystal on the 20 mesh screen sieve at the initial time.

The particle size of raw materials was found to contribute to less salting out. Present research found that >20 meshes milled raw materials was sufficient for production process which affected on 0% retained crystal on the 20 mesh screen sieve. The result agreed with that of Sawyer Jr. (1991); Aijala and Ahlnas (1998) who found that the appropriate particle size of raw materials were 35 meshes and 18-140 meshes that resulted on the less salting out.

Moreover, the particle size of milled raw material of >20 meshes could be trapped by hollows of 3 dimension network of xanthan gum solution (NQF-AGRO, 2001; Aimtrakarn *et al.*, 2011) and affected on small amount of weakly intermolecular force which were electrostatic attraction, van der Waals force and hydrogen bond. The large particle size would affect on bigger amount of weakly intermolecular force than that of small particle size (Sirimungkala, 2012; Anuragudom, 2012). Chance of a large agglomerate crystal formation of non-dissolved raw material in the suspension was less because of small amount of weakly intermolecular force in them.

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Table 24 Effects of suspending agent and temperatures of solution on salting out of 25-7-7 analysis grade of suspension fertilizer

Suspending agent (% xanthan gum)	Temperatures (°C)		G-average
	T1 (30-40)	T2 (50-60)	
	Salting out (% retained crystal)		
G1 (2.5)	0	0	0
G2 (3.0)	0	0	0
G3 (5.0)	0	0	0
T-average	0	0	0
F-Test	T	G	TG
	-	-	-
C.V. (%)			

Note: Means in a column and a row followed by the same letter are not significantly different, * significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

Nevertheless, the present research had found that the composition of 25-7-7 suspension at 30-40°C temperature were 54.3% urea, 4.13% KCl and 13.5% MKP, compared with a critical data that showed each raw material in saturated solution at 29°C which affected on non-salting out. The percentages raw materials in each were not greater than 57.6% urea, 28.3% KCl and 21.1% MKP respectively, (Wolf *et. al.*, 1985) and 24-8-8 grade of suspension which was made from liquid raw materials: APP (12-38-0), UAN (32%N), KCl, 1% clay, 0.3% H_2SiF_6 gave low viscosity 300-800 mPa.s which effected on 0% salting out (Jones and Stinson, 1983).

Temperatures of the solution

In case of desirable temperatures of solution (30-40°C and 50-60°C), results were in Table 21-24. These temperature ranges would be used for formulating suspension fertilizers in each condition. The 30-40°C temperature of solution treated

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with 2.5% xanthan gum had resulted in appropriate viscosities of 1633-1659 mPa.s while the 50-60°C temperature with 3% xanthan gum gave the appropriate viscosities of 2930 mPa.s and these also affected on acceptable pour-ability of 3-3.5, and 4.6% the remaining products, respectively, excellent stability of 100% apparent solids and acceptable salting out of 0% retained crystal.

The 30-40°C temperature of solution with 2.5% xanthan gum was preferable for formulating the suspension fertilizers because the temperature was found to reduce the size of crystals of the materials in the suspension and the results were in line with previous research of Slack and Walters (1963) who found that the 60-96°C temperature of solution resulted in 3.3% retained large crystal on 20 mesh test sieve causing the nozzle clogged. When the temperature was rapidly reduced to 29°C, the crystals were small. Furthermore, Richard and Charles (1976) found that the formulated suspensions with temperature 38°C and pH 6-6.5 were good storage conditions for shipment. Moreover, the temperature 30-40°C with 2.5% xanthan gum imparted to its physical parameters as follow, 1) pH: 5.57, 2) specific gravity: 1.229, 3) stability: 100% apparent solids at the initial time, 4) pour-ability: 3% the remaining products, 5) viscosity: 1633 mPa.s, 6) salting out: 0% retained crystal on the 20 mesh screen sieve.

Suspending agents

The concentration of suspending agent (Xanthan gum) affected on various viscosity of the suspensions (Table 21-24). The suspensions treated by temperature of solution 30-40°C or 50-60°C with 2.5% xanthan gum gave the viscosity of 1633-1659 mPa.s and pour-ability of 3-3.5% the remaining product. Those physical parameters were sufficient and non-significantly different in both viscosity (CIPAC, 2009c; Davenport *et. al*., 1978) and pour-ability (CIPAC, 2009a; Salladay and Kachelman, 1986). The selected temperature of solution of 30-40°C with 2.5% xanthan gum was more appropriate treatment because the treatment components could affect on reducing large crystals of the materials in suspension (Slack and Walters, 1963; Richard and Charles, 1976). Besides, the remaining treatments were insufficient

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in both viscosity and pour-ability. So the appropriate concentration of suspending agent for formulating 25-7-7 analysis grade of suspension fertilizers through solid raw materials was 2.5% Xanthan gum.

Production method

According to the investigation of all parameters, 25-7-7 analysis grade of suspension fertilizer production method could be suggested two methods. The first method consisted of 30-40°C temperature of solution using xanthan gum of 2.5% by total weight and the second method was of the 50-60°C temperature of solution with 2.5-3% xanthan gum by total weight. Both of them had to employ the milled solid raw materials in particle size of >20 meshes with 1280 rpm speed of agitator in the first stage and 2620 rpm speed of agitator in the second stage.

The appropriate treatments in the first method consisted of the following: 1) the amounts of 56.1 g water (25.5%) and 72.1 g urea 1(32.8%) in the clear liquid mixed solution stage (the first stage) with 1280 rpm speed of agitator, 2). the amounts of 5.5 g xanthan gum (2.5%), 9.1 g KCl (4.1%), 29.7 g MKP (13.5%) and 47.5 g urea 2 (21.6%) in the suspended solution stage (the second stage) with 2620 rpm speed of agitator respectively, and 3) the temperature of solution of 30-40°C. All of them had affected on the appropriate parameters of physical properties, the pH of 5.57, the SG of 1.229, the stability of 100% of apparent solids, and the pour-ability of 3% the remaining products, viscosity of 1633 mPa.s and salting out of 0% the retained crystals on the 20 mesh screen of test sieve. The present research results were similar to that of the 24-8-8 grade of suspension fertilizer produced using liquid raw materials, APP (12-38-0), UAN (32%N), KCl, 1% clay, 0.3% H_2SiF_6 that gave the low viscosity of 300-800 mPa.s with 0% in both pour-ability and salting out (Jones and Stinson, 1983). The 21-7-7 grade of suspension fertilizer produced from liquid raw materials, 20.6% APP (10-34-0), 66.1% UAN (28% N), 11.3% KCl and 2% clay also had the effect on appropriate suspension (Wolf *et. al*., 1985).

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The appropriate method for the 25-7-7 analysis grade of suspension fertilizer production using solid raw materials was following: 1) the use of >20 meshes milled raw materials of 54.4% urea, 4.1% KCl, and 13.5% MKP, 2) the total amount of raw materials was divided into 2 parts, the first for completely dissolved in the clear liquid mixed solution stage and the second for suspended in suspension solution stage, 3) the 30-40°C temperature of the solution, 4) the 2.5% xanthan gum suspending agent with 25.5% water, 5) the 1280 rpm speed of agitator for clear liquid mixed solution stage and 2620 rpm for the suspended solution stage, and 6) various appropriate physical properties of pH 5.57, SG of 1.229, viscosity of 1633mPa.s, the stability of 100% of apparent solids, pour-ability of 3% of remaining products, and the 0% salting out the retained crystals on the 20 mesh screen of test sieve. Thereby, all of the solid raw materials could be used for suspension fertilizer production instead of using liquid raw materials. The received suspension fertilizer production method was named Luxen's method.

Experiment 3

The results showed that all of 6 treatments were non-caking, homogenized, suspended fertilizers. The solutions were suspended by xanthan gum. They were consisted of needle crystals of urea 1 which were 100 µm width and 2,000 µm length, the suspended urea 2, suspended KCl, suspended MKP and suspended liquid (**Figure 34, 35 and 37**).

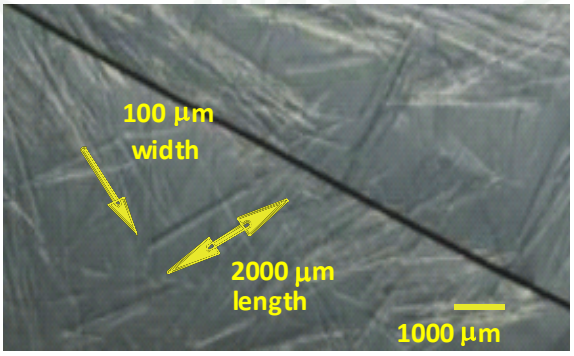

Figure 37 The measured needle crystal of urea 1 from 25-7-7 grade

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All of 6 treatments in this research were significantly different in the physical properties except pH, specific gravity and salting out (**Table 25**).

pH and **Specific gravity (SG)**

From **Table 25**, the many as pH and Specific gravity of all 6 treatments which were non-significantly different varied from 5.5-5.6 and 1.249-1.274, respectively.

Viscosities

From **Table 25**, the evaluations for viscosities in the suspension fertilizers processed by Luxen's Method by storage the suspension at various periods in normal room temperature were found that the suspensions were stored at 0-7, 15-30, 90, and 180 d yielded significantly different in viscosity. Tr_1 and Tr_2 yielded the lowest viscosity of 1445-1887 mPa.s. Tr_3 and Tr4 yielded the medium viscosity of 2832-3196 mPa.s. At the same time Tr_5 and Tr_6 yielded the highest viscosity of 15195, and 16316 mPa.s.

It could be noticeable that the increased stored periods affected on the increasing viscosities. These were described by the structure of suspension fertilizer in **Figure 38**.

Structure of suspension fertilizer

In 25-7-7 analysis grade of suspension fertilizer (**Figure 38**), they were consisted of water, xanthan gum , non-dissolved raw materials (urea 2, MKP and KCl) and needle crystals of urea 1. All of them linked together with variously attractive forces.

After the Xanthan gums were fed into the urea 1 solution in clear liquid mixed solution stage, they linked to water molecules in the solution with hydrogen bond to form in 3 dimension networks of xanthan gum solution.

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As processing, the suspensions which were consisted of xanthan gums, dissolved and non-dissolved raw materials were being agitated. The chains of polymer could not form in high three dimensional networks immediately. They were ordered arrangement which effected on low physical forces (intermolecular force, Van der Waals force and hydrogen bond) in the suspensions. Therefore, the measured viscosities by Brookfield Viscometer at initial time were low. When the suspensions were stored (the agitating removed) at variously given times (0, 7, 15, 30, 90 and 180 days), the bond formations were going to occur in xanthan gum solution, there had more amounts of physical forces among them which affected on formation of big agglomerates (high entanglement density) of three dimensional networks which were deranged because the suspensions were non-Newtonian fluids and pseudo-plastic fluid which effected on Thixotropic Flow Behavior (Aimtrakarn *et al*., 2011). So the high entanglement density of xanthan gum polymer was depended on the increasing stored periods (Thixotropic Flow Behavior) which were related to the research of Sawyer, Jr (1991) who found that viscosity increased along the increasing stored time. They effected on both high viscosity and suspended solution which suspended the non-dissolved raw materials for non-sediment. So the measured viscosities at variously given periods were high. They were related to the research of Sawyer Jr (1991) who found that a treated suspension fertilizer by some shear stress effected on being reduced viscosity to low one and Aimtrakarn *et al*. (2011) who noted that in Thixotropic Flow Behavior, it took more times to reversion of big agglomerates by random brownian movement.

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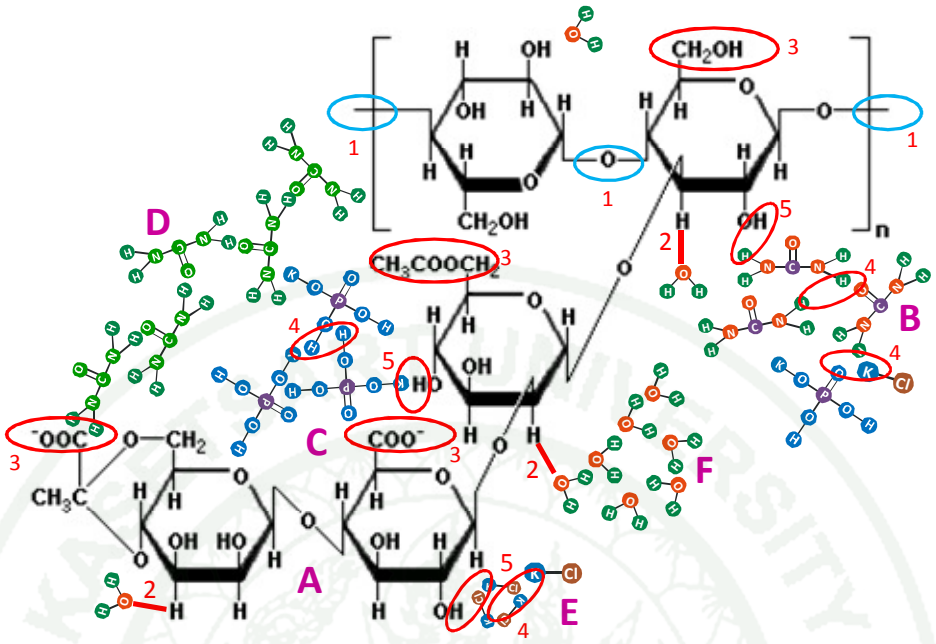

Figure 38 Structure of suspension fertilizer, linkage among xanthan gum, H_2O, non-dissolved raw materials: urea 2, KH_2PO_4 and KCl and needle crystals of urea 1, A = xanthan gum, B = urea 2, C = KH_2PO_4, D = needle crystals of urea1, E = KCl, F = H_2O, 1 = covalent bond, van der Waals force: 2 = hydrogen bond, 3 = carboxyl group, 4 = intermolecular force, 5 = hydroxyl group

Source: modified from Anil (2012)

Moreover, the suspension fertilizer is non-Newtonian fluid and pseudo-plastic fluid type (Aimtrakarn *et al.*, 2011) which effect on thixotropic behavior in suspension. As the suspensions being agitated in the suspended solution stage, they exhibited low viscosities because of 3 dimension networks of xanthan gum solution being ranged (low entanglement density of xanthan gum polymer). Then, at the finished process (the agitating removed), the bond formations being occurred, the suspensions were isotropic system which effected on low viscosities. The viscosity changed in terms of the changes from a single phase, isotropic system to two phase mixed isotropic/anisotropic system, and then a single phase anisotropic system at high concentration and to rest undisturbed for long time like as a recovery in thixotropic

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behavior, at last, the high viscosity in the suspensions (**Figure 20**; Oertel and Kulicke, 1991). They were related to research of Milas *et al*., (1985) who found that under the influence of shear, xanthan is pseudoplastic and exhibits very low viscosity at high shear rates.

Therefore, the measured viscosity was detected by using more than shear rates in Brookfield viscometer which effected on high viscosity because of all of the attractive forces being destroyed by the more than shear rates.

So Tr_1 and Tr_2 which were stored within 7 days were the appropriate treatments because their viscosities were 1445 and 1887 mPa.s which were related to the research of Salladay and Kachelman (1986) who found that viscosity was depended on analysis grade of suspension fertilizers and concentrations of suspending agent, which were 100-2000 mPa.s in appropriate limits.

Stability

From **Table 25**, the evaluations for stability in the suspension fertilizers processed by Luxen's Method by storage the suspension at various periods in normal room temperature were found that the suspensions were stored at 0-7, 15, 30, 90-180 d yielded significantly different in stability.

Tr_1 and Tr_2 yielded the highest stability of 100% apparent solid. Tr_3 yielded the stability of 99.62% apparent solid. Tr_4 yielded the stability of 98.75% apparent solid. Tr_5 and Tr_6 yielded the stability of 98.54 98.66% apparent solid. The stability of 99.62% apparent solid meant there were amounts of 0.38% supernatant that was amount of 0.38% the clear liquid on the top of the suspension fertilizer.

The results were compared to the acceptable limits of stability showed that the suspensions which were stored within 7 days were excellent stability, furthermore, the suspensions which were stored at interval between 15-180 days were very good stability (Browder and Ulmer, 1971).

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It could be noticeable that the increased stored periods affected on the decreasing stability (low apparent solids but high supernatant). These were described by the structure of supernatant in **Figure 38**.

From **Figure 38**, there were 5 types of attraction forces (1 = covalent bond, van der Waals force: 2 = hydrogen bond, 3 = carboxyl group, 4 = intermolecular force, 5 = hydroxyl group) in the structure of suspension fertilizer. All of components were weakly cross linked among them by those attraction forces in the suspension.

According to the gravitational force and long stored period, the finished products stored undisturbed for a long periods, the hydrogen bonds (**Figure 38)** which cross linked between water molecules and xanthan gums were destroyed by the gravitational forces. The separated water molecules floated on the top of the suspensions. The longer stored periods increased the quantity of separated water molecules. The more amounts of clear liquids could be observed at the top of suspension. Moreover, the unpublished preliminary investigation in suspending agents of my research, the suitable concentration of suspending agents would effect on the appropriate supernatant in suspensions. The research of Sawyer Jr (1991) who found that the shrinkage of gel and insufficient of suspending agents increased the quantity of supernatant in the suspension.

Pour-ability

From Table 25, the evaluations for pour-ability in the suspension fertilizers processed by Luxen's Method by storage the suspension at various periods in normal room temperature were found that the suspensions were stored at 0-7, 15- 90 and 180 d yielded significantly different in pour-ability.

Tr_1 and Tr_2 yielded the high pour-ability of 3.19-3.29% the remaining products. Tr_3, Tr_4 and Tr_5 yielded the pour-ability of 4.09-4.71% the remaining products. Tr_6 yielded the low pour-ability of 4.97% the remaining products. The results were compared to the acceptable limits of pour-ability which were not more

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than 5% of the remaining products (CIPAC, 2009a; Salladay and Kachelman, 1986) showed that all of treatments were acceptable.

It could be noticeable that the long stored periods of the products tended to have effected on low pour-ability of suspensions (high % of the remaining products). The suspensions with the high treated xanthan gums were difficult to be poured clearly. They were high viscous liquids (high viscosity). The more amounts of the remaining products were always stuck on the wall of the bottle which resulted in the more amounts of % the remaining products. They were described by structure of suspension fertilizer in **Figure 38**.

From **Figure 38**, there were 5 types of attraction forces (1 = covalent bond, van der Waals force: 2 = hydrogen bond, 3 = carboxyl group, 4 = intermolecular force, 5 = hydroxyl group) in the structure of suspension fertilizer. All of components were weakly cross linked among them by those attraction forces in the suspension.

Thereby, the suspension fertilizer was non-Newtonian fluid and pseudo-plastic fluid type (Aimtrakarn *et al*., 2011) which effect on thixotropic behavior in suspension. As the suspensions being agitated in the suspended solution stage, they exhibited low viscosities because of 3 dimension networks of xanthan gum solution being ranged (low entanglement density of xanthan gum polymer). Then, at the finished process (the agitating removed), the bond formations being occurred, it took more times to rebuild high 3-dimension networks (big agglomerates or high entanglement density) like as recovery in thixotropic behavior in suspension. They were related to the research of Sawyer Jr (1991) who found that a treated suspension fertilizer by some shear stress effected on being reduced viscosity to low one and Aimtrakarn *et al*. (2011) who noted that in Thixotropic Flow Behavior, it took more times to reversion of big agglomerates by random brownian movement. The high treated Xanthan gums which were employed in suspension fertilizer affected on high entanglement density of xanthan gum polymer (high 3 dimension network) because of cross linkage between the xanthan gum and the components in solution by more amounts of van der Waals forces (**Figure 38**).

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These researches were related to 24-8-8 grade of suspension which was made from liquid raw materials: 12-38-0, UAN (32%N), KCl, 1% clay, 0.3% H_2SiF_6 gave low viscosity: 300-800 cps which effected on high pour-ability (0% of the remaining products) (Jones and Stinson, 1983).

Salting out

From **Table 25**, the evaluations for salting out in the suspension fertilizers processed by Luxen's Method by storage the suspension at various periods in normal room temperature were found that all of suspensions did not yield in salting out.

All of treatments yielded 0% of retained crystal on the 20 mesh screen sieve (**Table 25**). The 0% salting out meant there had no retained crystals on 20 mesh screen of the test sieve. All of treatments were appropriate suspensions which were compared with the acceptable limits: maximum 2% retained crystals on a 20 mesh sieve (CIPAC, 2009b; Byrd and Scott, 1979).

These were described that all of treatments were treated by Luxen's method that were the solution temperature of 30-40°C, the milled raw materials in particle size of > 20 meshes, and the suspending agent of 2.5% xanthan gum. That temperature: 30 to 40°C effected on the small crystals of nutrient materials in suspension which related to many researches of Slack and Walters (1963); Kendrick, Jr (1974); Fox and Oldland (1976) who found that the temperature of solution 29°C, 38°C and 70°C to 82°C affected on the small crystals of nutrient materials in the suspension fertilizers, respectively. Furthermore, Johnson and Huber (1991) who found that a suspension with sufficient gel strength would support the solids contained in the suspension and prevented them from setting out. So the suitable suspending agent for this research was 2.5% xanthan gum for the suspensions which gave 0% of retained crystal on the 20 mesh screen sieve at variously stored periods.

The particle size of raw materials contributes to less salting out. In these researches, more than 20 meshes milled raw materials were enough to be employed in

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the process which affected on 0% of retained crystal on the 20 mesh screen sieve. They were related to Sawyer, Jr (1991); Aijala and Ahlnas (1998) who found that the appropriate particle size of raw materials were 35 meshes and 18-140 meshes, respectively, that effected on the less salting out.

Moreover, the particle size of milled raw materials which was >20 meshes and could be trapped by hollows of 3 dimension network of xanthan gum solution (NQF-AGRO, 2001; Aimtrakarn *et al*., 2011) effected on less amounts of weakly intermolecular force which were the electrostatic attraction, van der Waals force and hydrogen bond. The big particle size effects on more amounts of intermolecular force than small particle size (Sirimungkala, 2012; Anuragudom, 2012). Chance of formation in big agglomerates from the non-dissolved raw materials is less because of less amounts of intermolecular force in them.

Nevertheless, the raw material composition of 25-7-7 at 30-40°C in these researches, which was 54.3% urea, 4.13% KCl and 13.5% MKP were related to the raw material composition of 21-7-7 at 29°C which was not greater than in each of 57.6% urea, 28.3% KCl, 21.1% MKP respectively, which non-effecting on salting out (Wolf *et. al*., 1985) and 24-8-8 grade of suspension which was made from liquid raw materials: APP (12-38-0), UAN (32%N), KCl, 1% clay, 0.3% H_2SiF_6 gave 300-800 cps viscosity which effected on 0% salting out (Jones and Stinson, 1983).

Relation among viscosity, stability, pour-ability, and salting out

From the mentioned physical parameters (viscosity, stability, pour-ability, and salting out) above, it could be noticeable that the viscosity was major appropriateness which affected on good suspension fertilizers. The viscosity influenced to stability, pour-ability, and salting out. The inadequate viscosity such as lower or higher viscosity effects on the remaining physical parameters in unsuitableness such as high supernatant, big agglomerates, poor pour-ability, high remaining products in pour-ability, and high retained crystals on 20 mesh sieve. In contrast, the sufficient concentration of the suspending agent effects on appropriate viscosity which would

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effects on suitable stability, suitable pour-ability and suitable salting out at variously stored periods. So before processing a suspension fertilizer, it has to do a preliminary research in concentrations of the suspending agent for receiving a good suspension.

Table 25 Treatments and the evaluated physical properties of 25-7-7 analysis grade of suspension fertilizer

treatment	Physical property					
	pH	S.G.	Viscosity (mPa.s[1/])	Stability (%[2/])	Pour-ability (%[3/])	Salting out (%[4/])
Tr_1(0 d)	5.6	1.263	1445 d[5/]	100.0 a[5/]	3.19 c[5/]	0
Tr_2(7 d)	5.5	1.274	1887 d	100.0 a	3.29 c	0
Tr_3(15 d)	5.5	1.252	2832 c	99.62 b	4.09 b	0
Tr_4(30 d)	5.6	1.267	3196 c	98.75 c	4.50 ab	0
Tr_5(90 d)	5.5	1.257	15195 b	98.66 cd	4.71 ab	0
Tr_6(180 d)	5.5	1.249	16361 a	98.54 d	4.97 a	0
F-Test	ns	ns	*	*	*	-
C.V. (%)	2.3	1.1	6.2	0.1	10.2	

Note: SG= specific gravity

[1/] by Brook field viscometer, spindle # 3 and 4, 30 rpm, time 2 minute

[2/] % of the apparent solids, [3/] % of the remaining products

[4/] % of the retained crystals on the 20 mesh screen of test sieve.

[5/] Means in a column followed by the same letter are not significantly different

* significantly different, ns = non-significantly different, according to LSD (p=0.05)

25-7-7 analysis grade of suspension fertilizers which were processed by Luxen's method was a non-Newtonian fluid, pseudoplastic fluid type, thixotropy, pH of 5.6 and specific gravity of 1.274. The stored periods effected on viscosity that increased along the increasing stored periods, effected on very good to excellent

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stability and acceptation in both pour-ability and salting out. Thereby, they have high efficiency in physical properties within 180 days of stored time at normal room temperature.

Experiment 4

All of treatments showed non-caking, homogenized and suspended fertilizers.

Chemical properties

From **Table 26**, the suspension fertilizers that processed by Luxen's Method were analyzed for nutrient concentration in the suspensions after they had been stored at 180 d in normal room temperature. It was found that all of the suspension fertilizers showed non-significantly different in nutrient concentration to the nutrient concentrations that were firstly calculated.

Table 26 Treatments showed the concentrations of N, P_2O_5 and K_2O in their suspension fertilizers after having been stored at 180 d

Suspension fertilizer grade	Concentration of nutrient in the suspension		
	% N	% P_2O_5	% K_2O
25-7-7 (Gr1)	25.05 a	7.10 f	7.03 f
20-10-10 (Gr2)	20.00 b	9.78 e	10.08 e
12-24-12 (Gr3)	12.35 e	24.25 a	12.10 d
13-13-21 (Gr4)	13.15 d	13.28 d	20.80 b
7-21-21 (Gr5)	7.23 f	20.88 b	21.03 a
15-15-15 (Gr6)	15.05 c	15.10 c	15.00 c
F-test	*	*	*
C.V. (%)	0.91	1.32	0.69

Note: Means in a column and a row followed by the same letter are not significantly different, * Significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

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25-7-7 (Gr1) showed 25.05% N, 7.10% P_2O_5 and 7.03% K_2O. At the same time 20-10-10 (Gr2) showed 20.00% N, 9.78 % P_2O_5 and 10.08 % K_2O. It was noticeable that 9.78 % P_2O_5 of 20-10-10 (Gr2) was lower than 10% P_2O_5 that was firstly calculated because of un-satisfactory sampling affecting on error value of nutrient concentration and the suspension fertilizers were mixed liquid fertilizer consisted of solid raw materials. However, the error value was acceptable to the element deviation limit of Department of Agriculture. They were related to the 20.80% K_2O of 13-13-21 (Gr4) and the 20.88% P_2O_5 of 7-21-21 (Gr5).

pH

From **Table 27**, the evaluations for pH in the suspension fertilizers processed by Luxen's Method were found that the fertilizer grades yielded significantly different in pH. While the various stored periods and the interaction between them yielded non-significantly different in pH of 5.26-5.27, and 4.7-5.6 respectively.

The fertilizer grade factor gave significantly different in average pH. 20-10-10 fertilizer grade gave the highest average pH of 5.62. 12-24-12 fertilizer grade gave the lowest average pH of 4.84. 13-13-21 and 25-7-7 fertilizer grade gave average pH of 5.26 and 5.53 respectively. 7-21-21 and 15-15-15 fertilizer grade gave the same average pH of 5.18.

It was revealed that the concentration and kinds of solid raw materials in the individual suspension were unequal which affected on total of solubility of solid raw materials in those suspensions in difference. Each solid raw material gave difference in both solubility and pH in the suspension (**Table 27**; **9**).

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Table 27 Effects of fertilizer grades and stored periods on pH

Suspension fertilizer grade	Stored periods (day)				Gr-average
	D0	D30	D90	D180	
	pH				
25-7-7 (Gr1)	5.5	5.5	5.5	5.5	5.53 W
20-10-10 (Gr2)	5.6	5.6	5.6	5.6	5.62 V
12-24-12 (Gr3)	4.9	4.7	4.8	4.8	4.84 Z
13-13-21 (Gr4)	5.2	5.3	5.2	5.3	5.26 X
7-21-21 (Gr5)	5.1	5.2	5.1	5.2	5.18 Y
15-15-15 (Gr6)	5.1	5.1	5.2	5.2	5.18 Y
D-average	5.27	5.26	5.27	5.27	5.26
F-test	Gr		D		GrD
	*		ns		ns
C.V. (%)	1.39				

Note: Means in a column and a row followed by the same letter are not significantly different, * Significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

Specific gravity

From **Table 28**, the evaluations for specific gravities in the suspension fertilizers processed by Luxen's Method were found that the fertilizer grades yielded significantly different in specific gravities. While the various stored periods and the interaction between them yielded non-significantly different in specific gravities (1.372-1.376, and 1.237-1.433 respectively).

The fertilizer grade factors gave significantly different in average specific gravity. 13-13-21, 12-24-12 and 7-21-21 fertilizer grade gave the highest average specific gravity of 1.424-1.429. 25-7-7 fertilizer grade gave the lowest average

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specific gravity of 1.245. 20-10-10 and 15-15-15 fertilizer grade gave the medium average specific gravity of 1.321 and 1.396 respectively.

It was revealed that amounts and kinds of solid raw materials in the individual suspension were unequal (**Table 15**) which affected on difference in density of the suspensions (**Table 9**).

In this experiment we found that the ratio of total weight of raw materials (TWR, %) and total weight nutrient ratio (S-NPK, %) in the suspension involved specific gravity. The less value gave high specific gravity when it was compared with the value of 15-15-15 fertilizer grade (**Table 9; 15; 29**). Moreover, **Figure 39** showed regression line between TWR/S-NPK and specific gravity that could be forecasted a specific gravity of a suspension fertilizer.

Table 28 Effects of fertilizer grades and stored periods on specific gravity

Suspension fertilizer grade	Stored periods (day)				Gr-average
	D0	D30	D90	D180	
	Specific gravity				
25-7-7 (Gr1)	1.237	1.247	1.250	1.246	1.245 Z
20-10-10 (Gr2)	1.318	1.319	1.327	1.319	1.321 Y
12-24-12 (Gr3)	1.428	1.428	1.427	1.427	1.428 W
13-13-21 (Gr4)	1.425	1.421	1.424	1.425	1.424 W
7-21-21 (Gr5)	1.431	1.426	1.429	1.433	1.429 W
15-15-15 (Gr6)	1.395	1.398	1.398	1.394	1.396 X
D-average	1.372	1.373	1.376	1.374	1.373
F-test	Gr		D		GrD
	*		ns		ns
C.V. (%)	0.65				

Note: Means in a column and a row followed by the same letter are not significantly different, * Significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

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Table 29 Ratio of total weight of raw materials (TWR, %) and total weight nutrient ratio (S-NPK, %) in suspension involved specific gravity

Fertilizer grade	TWR/S-NPK	Evaluated value	Specific gravity
25-7-7	74.50/39	1.910	1.245
20-10-10	71.45/40	1.786	1.321
15-15-15	73.59/45	1.635	1.396
13-13-21	76.09/47	1.618	1.424
12-24-12	73.95/48	1.540	1.428
7-21-21	70.22/49	1.433	1.429

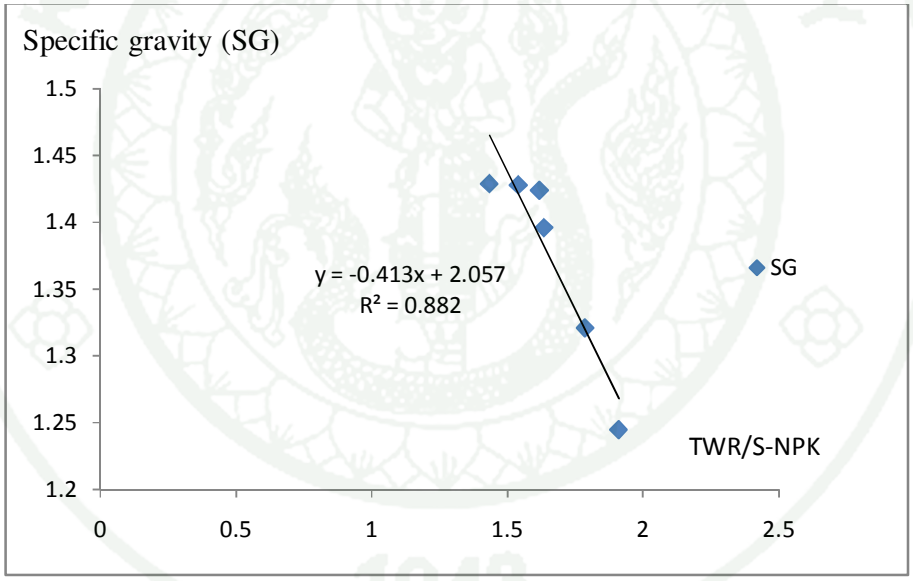

Figure 39 Regression line between TWR/S-NPK and specific gravity
TWR= total weight of raw materials
S-NPK= total weight of nutrients ratio

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Viscosity

From **Table 30** and **Figure 40,** the evaluations for viscosities in the suspension fertilizers processed by Luxen's Method were found that the fertilizer grades, the various stored periods and interaction between them yielded significantly different in viscosities.

The fertilizer grades gave significantly different in average viscosity. The 12-24-12, 15-15-15, 20-10-10 and 25-7-7 fertilizer grade gave the highest average viscosity of 6826-9375 mPa.s. The 7-21-21 and 13-13-21 fertilizer grade gave the lowest average viscosity of 3729-4181 mPa.s.

The stored periods gave significantly different in average viscosity. The suspension fertilizers stored at 0 and 30 d gave non-significantly different average viscosity of 1534-2325 mPa.s, however, they were significantly different to the suspension fertilizers stored at 90 and 180 d gave non-significantly different average viscosity of 11070-11877 mPa.s.

The interactions between the fertilizer grade and the stored periods that gave significantly different viscosity were found that all of the fertilizer grades stored at 0 and 30 d gave non-significantly different in the lowest viscosity of 853-3249 mPa.s. Furthermore, the 12-24-12, 15-15-15, 20-10-10 and 25-7-7 grade stored at 90 and 180 d gave non-significantly different in the highest viscosity of 11329-16635 mPa.s. At the same time 7-21-21 and 13-13-21 grade stored at 90 and 180 d gave non-significantly different in the medium viscosity of 6155-7419 mPa.s. However, those three viscosities were significantly different.

So before processing a new suspension fertilizer, in preparing documents it must be known a viscosity at 90 d stored period of the new suspension by forecasting with regression line in **Figure 43-45,** the received pour-ability of a new suspension could be indicated a suitableness of the new suspension (it would be described later).

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It could be noticeable that the suspensions: 25-7-7, 20-10-10, 12-24-12, and 15-15-15 gave viscosity of 9375, 8104, 7994 and 6826 mPa.s, respectively, which were compared with the viscosity of 4181 and 3729 mPa.s of the suspensions: 13-13-21 and 7-21-21, respectively, were found that high consumption in urea components (**Table 31**) in the suspension affected on high viscosity because the more amounts of urea molecules could attract to the other molecules of urea, non-dissolved raw materials, even, the hollow of 3 dimension networks of xanthan gum in suspension, with more amounts of NH- group (amide group) in urea molecules by more intermolecular force (NQF-AGRO, 2001).

Table 30 Effects of fertilizer grades and stored periods on viscosity

Suspension fertilizer grade	Stored periods (day)				Gr-average
	D0	D30	D90	D180	
	Viscosity (mPa.s)[1/]				
25-7-7 (Gr1)	2144 f	3249 f	15471 ab	16635 a	9375 X
20-10-10 (Gr2)	1854 f	2808 f	13374 bcd	14380 abc	8104 XY
12-24-12 (Gr3)	1570 f	2379 f	11329 d	12026 cd	6826 Y
13-13-21 (Gr4)	956 f	1449 f	6899 e	7419 e	4181 Z
7-21-21 (Gr5)	853 f	1292 f	6155 e	6618 e	3729 Z
15-15-15 (Gr6)	1829 f	2771 f	13193 bcd	14186 abc	7994 Y
D-average	1534 B	2325 B	11070A	11877 A	6702
F-test	Gr		D		GrD
	*		*		*
C.V. (%)	27.9				

Note: [1/] by Brook field viscometer, spindle # 3 and 4, 30 rpm, time 2 minute

Means in a column and a row followed by the same letter are not significantly different, * Significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

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Furthermore, the lower than 15% K_2O in the suspension gave high viscosity because of more amounts of urea consumption which had more amounts of NH- groups affecting more both van der Waals force and viscosity at last (**Table 31**). In contrast, the higher than 15% K_2O in the suspension gave low viscosity because of less amounts of urea consumption. The larger the amount of K-salt consumption the less the amounts of urea consumption was. Non-dissolved particle of MKP and KCl in suspension had less amounts of intermolecular force than urea because of them having no NH- group.

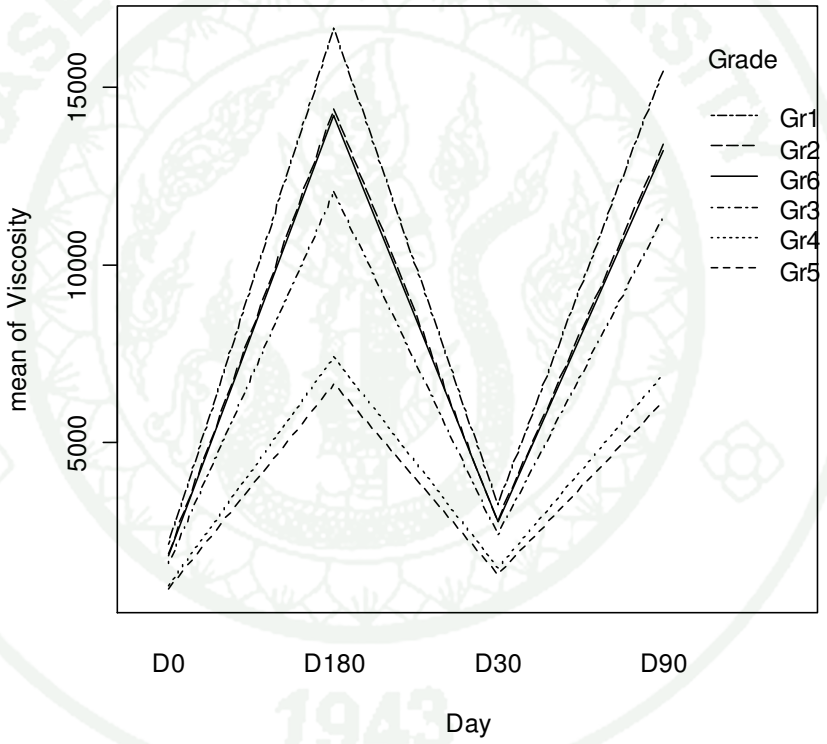

Figure 40 Plotting of interaction between stored periods and fertilizer grade on viscosity

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Table 31 Components of the suspensions: % urea, % gum and % (MKP+KCl) affecting on various viscosities at various periods, urea be arranged in order of amounts of urea

Treatments				Stored periods (days)				
ratio	urea (%)	gum (%)	MKP +KCl (%)	D0	D30	D90	D180	Gr average
				Viscosity				
25-7-7 (Gr1)	54.4	2.5	17.6	2144	3249	15471	16635	9375 X
20-10-10 (Gr2)	43.5	3.0	25.0	1854	2808	13374	14380	8104 XY
15-15-15 (Gr6)	32.6	3.5	37.5	1829	2771	13193	14186	7995 Y
12-24-12 (Gr3)	22.5	3.0	30.1	1570	2379	11329	12026	6826 Y
13-13-21 (Gr4)	28.5	2.0	45.8	956	1449	6899	7419	4181 Z
7-21-21(Gr5)	15.2	2.5	52.5	853	1292	6155	6618	3729 Z
D average				1534 B	2325 B	11070 A	11877 A	

Stability

From **Table 32,** the evaluation for stability in the suspension fertilizers processed by Luxen's Method was found that the various stored periods yielded significantly different in stability. While the fertilizer grades and interaction between them yielded non-significantly different in stability.

The stored periods showed their means of significantly different in stability. The suspensions stored within 90 d gave average stability of 100.00% apparent solid. At the same time the suspensions stored at 180 d gave average stability of 99.65% apparent solid.

It was revealed that as the suspensions stored undisturbed for a longer period of time, the gravitational forces could destroy the van der Waals force that attracted water molecules and solid raw materials to xanthan gum in 3 dimension networks. The free water molecules (supernatant) floated up to the top of suspension.

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So the low urea component in any suspensions by comparing with the urea consumption of 25-7-7 had to be increased concentration of suspending agent, otherwise, a supernatant, liquid layer on bottom and salting out would occur in those suspensions (**Table 31**)

The % apparent solids of all suspension fertilizers compared with the acceptable limits were very good stability (Browder and Ulmer, 1971).

Table 32 Effects of fertilizer grades and stored periods on stability

Suspension fertilizer grade	Stored periods (day)				Gr-average
	D0	D30	D90	D180	
	Stability (% apparent solid)				
25-7-7 (Gr1)	100.00	100.00	100.00	100.00	100.00
20-10-10 (Gr2)	100.00	100.00	100.00	99.75	99.94
12-24-12 (Gr3)	100.00	100.00	100.00	99.73	99.93
13-13-21 (Gr4)	100.00	100.00	100.00	99.33	99.83
7-21-21 (Gr5)	100.00	100.00	100.00	99.33	99.83
15-15-15 (Gr6)	100.00	100.00	100.00	99.77	99.94
D-average	100.00A	100.00A	100.00A	99.65B	
F-test	Gr		D		GrD
	ns		*		ns
C.V. (%)	0.25				

Note: Means in a column and a row followed by the same letter are not significantly different, * Significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

Pour-ability

From Table 33 and Figure 41, the evaluation for pour-ability in the suspension fertilizers processed by Luxen's Method was found that the fertilizer grades, the

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various stored periods and interaction between them yielded significantly different in pour-ability.

The suspension fertilizer grades showed their means of significantly different pour-ability. The 20-10-10, 12-24-12, 15-15-15 and 25-7-7 fertilizer grade gave the same low average pour-ability of 3.20-3.65% remaining product. The 13-13-21 and 7-21-21 fertilizer grade gave the same high average pour-ability of 2.40-2.45% remaining product.

Table 33 Effects of fertilizer grades and stored periods on pour-ability

Suspension fertilizer grade	Stored periods (day)				Gr-average
	D0	D30	D90	D180	
	Pour-ability (% remaining product)				
25-7-7 (Gr1)	2.52 hijk	3.55 def	3.71 def	4.83 bc	3.65 X
20-10-10 (Gr2)	1.62 lm	2.28 ijkl	2.38 ijkl	6.51 a	3.20 Y
12-24-12 (Gr3)	2.52 hijk	3.56 def	3.73 de	3.38 efg	3.30 XY
13-13-21 (Gr4)	1.37 m	1.93 jklm	2.03 jklm	4.28 cd	2.40 Z
7-21-21 (Gr5)	1.78 klm	2.49 hijk	2.61 ghij	2.93 fghi	2.45 Z
15-15-15 (Gr6)	2.11 jklm	3.28 efgh	3.44 ef	5.28 b	3.53 XY
D-average	1.99 C	2.85 B	2.98 B	4.53 A	
F-test	Gr		D		GrD
	*		*		*
C.V. (%)	18.3				

Note: Means in a column and a row followed by the same letter are not significantly different, * Significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

The stored periods gave significantly different in average pour-ability. The suspensions stored at 0 d gave the highest average pour-ability of 1.99% remaining product. The suspensions stored at 180 d gave the lowest average pour-ability of

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4.53% remaining product. While the suspensions stored at 30 d and 90 d gave the same medium average pour-ability of 2.85-2.98% remaining product.

The interactions of all suspension between suspension fertilizer grade and stored periods showed significantly different pour-ability. The 20-10-10 suspension fertilizer grade stored at 180 d gave pour-ability of 6.51% remaining product which was significantly different pour-ability to the 13-13-21, 20-10-10, 7-21-21, 15-15-15, 12-24-12 and 25-7-7 suspension fertilizer grade stored at various periods gave the non-significantly different pour-ability of 1.37-5.28% remaining product.

The pour-ability of % remaining product of all suspension fertilizers compared with the acceptable limits of not more than 5% remaining product were acceptable (Salladay and Kachelman, 1986) except 20-10-10 and 15-15-15.

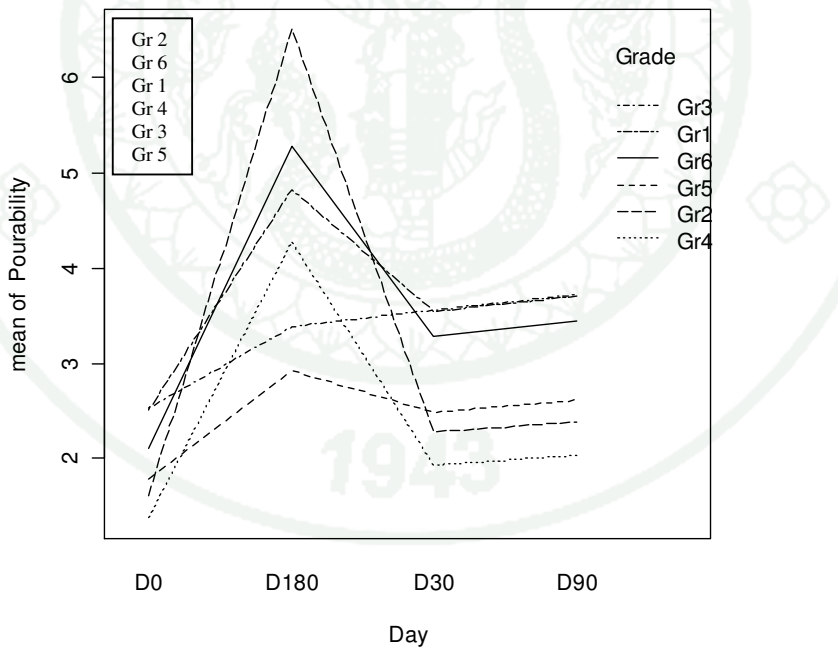

Figure 41 Plotting of interaction between stored periods and fertilizer grade on pour-ability

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So the suspensions stored for longer periods effected on low pour-ability of high % remaining product. They were revealed that the suspension were thixotropy which affected on reversible viscosity of the suspensions. After the suspension had been finished in process, water molecules, some raw materials and some needle crystals of urea 1 were attracted to xanthan gum by van der Waals forces in the suspensions. The longer the time, the greater the van der Waals forces were. Those forces affected on high viscosity that gave low pour-ability of high % remaining product.

Salting out

From **Table 34** and **Figure 42**, The evaluation for salting out in the suspension fertilizers processed by Luxen's Method were found that the fertilizer grades, the various stored periods and interaction between them yielded significantly different in salting out.

The 20-10-10 fertilizer grade gave average salting out of 0.13% retained crystal was significantly different to the average salting out of 0% retained crystal of the remaining fertilizer grades. The suspensions stored at within 90 d and at within 180 d gave average salting out of 0.00 and 0.09% retained crystal respectively. The 20-10-10 fertilizer grade stored at 180 d gave salting out of 0.51% retained crystal was significantly different salting out to the salting out of 0.00% retained crystal of the remaining fertilizer grades.

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Table 34 Effects of fertilizer grades and stored periods on salting out

Suspension fertilizer grade	Stored periods (day)				Gr-average
	D0	D30	D90	D180	
	Salting out (% retained crystal)				
25-7-7 (Gr1)	0.00 b	0.00 b	0.00 b	0.00 b	0.00 Y
20-10-10 (Gr2)	0.00 b	0.00 b	0.00 b	0.51 a	0.13 X
12-24-12 (Gr3)	0.00 b	0.00 b	0.00 b	0.00 b	0.00 Y
13-13-21 (Gr4)	0.00 b	0.00 b	0.00 b	0.00 b	0.00 Y
7-21-21 (Gr5)	0.00 b	0.00 b	0.00 b	0.00 b	0.00 Y
15-15-15 (Gr6)	0.00 b	0.00 b	0.00 b	0.00 b	0.00 Y
D-average	0.00 B	0.00 B	0.00 B	0.09 A	0.02
F-test	Gr		D		GrD
	*		*		*
C.V. (%)	132.2				

Note: Means in a column and a row followed by the same letter are not significantly different, * Significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

The salting out of % retained crystal of all suspension fertilizers compared with the acceptable limits of maximum 2% retained on a 20 mesh sieve were acceptable (Byrd and Scott, 1979).

In case of the 20-10-10 fertilizer grade with salting out: 0.51% retained crystal; it was revealed that the less amounts of xanthan gum effected on unsuitable suspension. The low density of entanglement of xanthan gum in the suspension was occurred. It was not enough to attract all of the raw materials into the hollow in 3 dimension networks. By the intermolecular forces among the raw materials, the remaining raw materials would form large crystals or large particles. The concentration of xanthan gum (4%) being used in this fertilizer grade was inadequate.

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It would be adjusted more amounts of xanthan gum (more amounts of 4% xanthan gum) for suitable suspension.

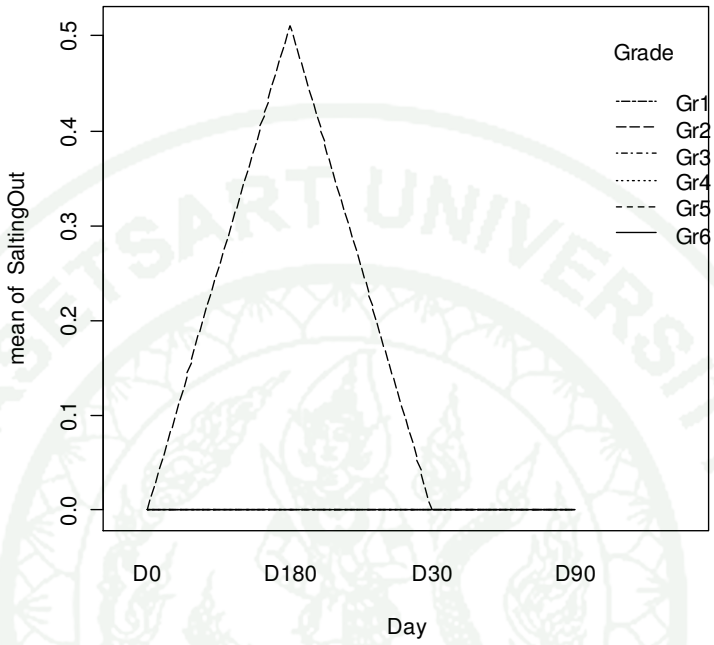

Figure 42 Plotting of interaction between stored periods and fertilizer grade on salting out

Relation of viscosity to some raw materials and pour-ability

Regression line

According to Figure 43 the regression line between % N ratio in the suspension and % used urea; if it knows a % N ratio in a suspension, the amount of used urea could be forecasted for trending process. From Figure 44 the regression line between percentage of sums of (MKP+KCl) and viscosity at 90 d stored period was plotted which could be forecasted a viscosity at 90 d stored period if it knows a percentage of sums of (MKP+KCl). The viscosity could forecast a pour-ability by the equation in the Figure 45 which was the regression line between pour-ability (%

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remaining product) and viscosity at 90 d stored period. The viscosity and pour-ability would indicate the suitableness of suspension before a process.

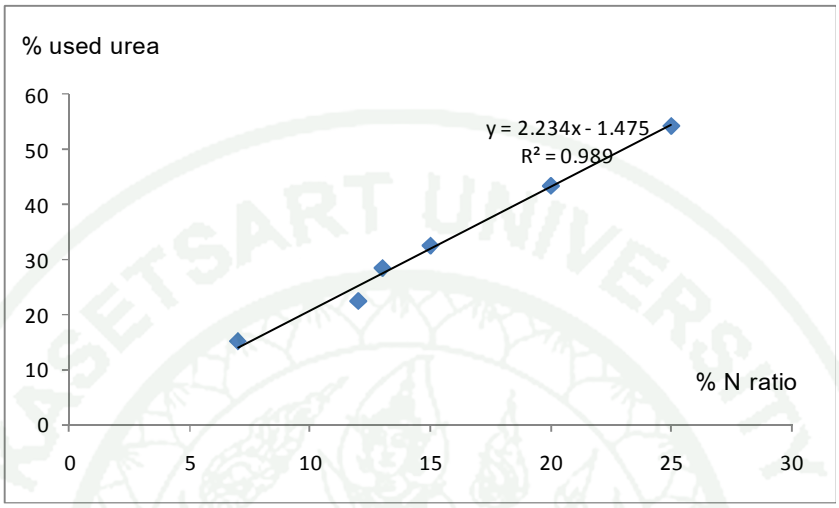

Figure 43 Regression line between %N ratio in a suspension and % used urea

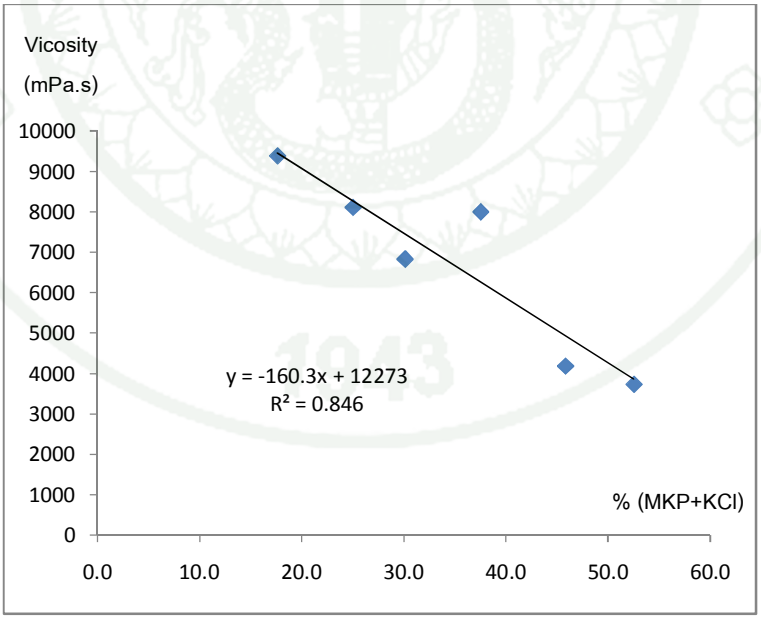

Figure 44 Regression line between % sum of (MKP+KCl) and viscosity at 90 d stored period

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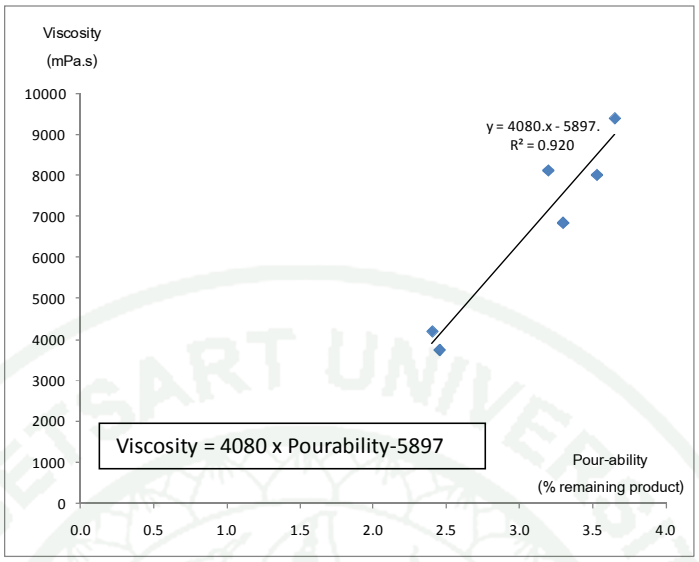

Figure 45 Regression line between pour-ability (% remaining product) and viscosity at 90 d stored period

From **Table 35,** it was concluded that Luxen's method which was consisted of >20 meshes of milled raw materials, speeds of agitator: 1820 and 2620 rpm, temperature of solution: 30-40^{0}C and suspending agent: xanthan gum could be processed the various analysis grades of suspension fertilizers such as high N ratio: 25-7-7 and 20-10-10, high P_2O_5 ratio: 12-24-12 and 7-21-21, high K_2O ratio: 13-13-21 and equal in NPK ratio: 15-15-15 with solid raw materials: urea, MAP, MKP, KCl and xanthan gum as suspending agent. The products gave appropriate chemical and physical properties such as accurate nutrient concentration, suitable in pH and specific gravity, fairly low viscosity, very good stability, acceptable in both pour-ability and salting out. The products could be stored for 180 days in normal room temperature without supernatant and poured easily.

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Table 35 The acceptably evaluated physical parameters of the suspension fertilizer grades

Fertilizer	Evaluated physical parameter					
Grade	pH	SG	Viscosity	Stability	Pour-ability	Salting out
25-7-7 (Gr_1)	5.53	1.315	9375	100.00	3.65	0.00
20-10-10 (Gr_2)	5.62	1.321	8104	99.94	3.20	0.13
12-24-12 (Gr_3)	4.84	1.428	6826	99.93	3.30	0.00
13-13-21 (Gr_4)	5.26	1.424	4181	99.83	2.40	0.00
7-21-21 (Gr_5)	5.18	1.429	3729	99.83	2.45	0.00
15-15-15 (Gr_6)	5.18	1.396	7994	99.94	3.53	0.00

Experiment 5

Physical and chemical properties of the soil base media after applications

From **Table 36**, according to the soil base media (soil: coconut coir: burned rice husk: rice husk =2:2:1:1 v/v), the analysis of physical and chemical properties of them after tested showed that the soil base media of the control were moderate alkaline (pH 8.14), the electrical conductivity (ECe) of 0.254 dS/m as non-saline soil and suitable for plant growth, organic matter (OM) of 12.12% as higher to suitable range of OM of 2.5-3% (It was noticeable that the high organic matter of 12.12% derived from coconut coir dust, burnt rice husk and rice husk), total % N of 0.152 as low nitrogen in soil fertility, available phosphorous, exchangeable potassium, exchangeable calcium and exchangeable magnesium were very high as 311, 577, 4985 and 406 mg/kg to suitable range as 26-42, 130, 1,040 and 135 mg/kg respectively.

From Table 37, the evaluations for efficiency in use of the suspension fertilizers processed by Luxen's Method were compared between the suspension fertilizers applied under drip fertigation and the granule fertilizer applied under broadcasting on Chinese kale in plastic pots. It was found that the soil base media

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showed the increasing electrical conductivity and the decreasing exchangeable calcium significantly. At the same time pH, organic matter (OM), total % N, available phosphorous, exchangeable potassium and exchangeable magnesium (Mg) showed non-significantly different in averages ($p \leq 0.05$).

Electrical conductivity (ECe)

From **Table 37**, the suspension fertilizers that were applied under drip fertigation at the rate of less than a half (Tr_3), greater than two times (Tr_5) and equal (Tr_4) to the granule fertilizer rate of use (Tr_2) affected on non-significantly different electrical conductivity (0.274-0.298 dS/m) to the control (Tr_1) (0.254 dS/m). But they were significantly different to Tr_2 that affected on increasing electrical conductivity significantly (0.484 dS/m). They were acceptable to non-saline soil and did not inhibit plant growth because of their electrical conductivity being not over to the suitable range of 2 dS/m (**Table 36**). The increasing electrical conductivity of the soil base media applied under granule fertilizers were extensively normal situation. It was noticeable that the electrical conductivity of all drip fertigation treatments (0.274-0.298 dS/m) was lower than the increasing electrical conductivity of Tr_2 (0.484 dS/m) significantly. It was reviewed that the suspension fertilizers were diluted with water to a uniform fertilizer solution. When they were dripped into the plant in the plastic pot, they dispersed to root area and leached to the bottom of the pot, at last they leaked out from the pot. The concentration of fertilizer solution on the soils in the pot was less amounts affected on low electrical conductivity.

Exchangeable calcium

The suspension fertilizers were applied under drip fertigation at the increased rate of use affected on decreasing exchangeable calcium significantly. At the same time the granule fertilizers were applied under broadcasting did not affect on exchangeable calcium (**Table 37**).

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Tr_3, Tr_4 and Tr_5 applied under drip fertigation at the suspension fertilizer rate of use of 882, 1764 and 3528 mg/pot respectively affected on the decreasing amounts of exchangeable calcium in the soils of 4171, 3482 and 2996 mg/kg significantly (**Table 36**). At the same time Tr_2 that was applied under broadcasting granule fertilizer did not affect on exchangeable calcium in the soils of 4913 mg/kg. Tr_1 that un-applied under both drip and broadcasting showed exchangeable calcium in the soils of 4985 mg/kg. The suitable range was 1,040 mg/kg.

These could be reviewed that in this research, watering amount of 200 ml to the pot twice a day affected on leaching the amount of exchangeable calcium from the soil in the pot. Moreover, the uniform fertilizer solution from drip fertigation system had enhanced more amounts of active ingredient immediately such as $H_2PO_4^{-2}$ that reacted to more amounts of exchangeable calcium in the soils easily. The resulted products could leach out of the soils in the pot. The concentration of exchangeable calcium was less amounts on the soils in the pot. The more amounts of the suspension fertilizers, the less amounts of exchangeable calcium in the soils were.

pH, organic matter (OM), total % N, available phosphorous, exchangeable potassium and exchangeable magnesium (Mg) showed non-significantly different in averages ($p \leq 0.05$).

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Table 36 Physical and chemical properties of soil base media after tested, compared with the suitable recommendation of Office of Agricultural Research and Development Region 1

Soil properties	Evaluated value					Suitable range[1/]
	After test					
	Tr_1	Tr_2	Tr_3	Tr_4	Tr_5	
pH (1:1)	8.14	7.77	6.91	7.17	7.17	6-7
Electrical conductivity (ECe; dS/m)	0.254	0.484	0.298	0.284	0.274	0-2
Organic matter (OM; %)	12.12	13.08	11.65	12.94	13.21	2.5-3.0
Total % N	0.152	0.128	0.112	0.104	0.104	0.3-0.6
Available phosphorous (mg/kg)	311	298	258	245	302	26-42
Exchangeable potassium (mg/kg)	577	618	532	550	575	130
Exchangeable calcium (mg/kg)	4985	4913	4171	3482	2996	1,040
Exchangeable magnesium (mg/kg)	406	423	405	395	389	135

Note: [1/] OARD 1 (2012)

Table 37 The evaluated chemical and physical properties of soils base media after tested

Treat-ments	Evaluated value							
	pH	EC (dS/m)	OM %	Total N %	Avail. P (mg/kg)	Exch. K (mg/kg)	Exch. Ca (mg/kg)	Exch. Mg (mg/kg)
Tr1	8.14	0.254 b	12.12	0.152	310.5	576.9	4984.6 a	406.2
Tr2	7.77	0.484 a	13.08	0.128	297.5	618.0	4913.1 a	423.1
Tr3	6.91	0.298 b	11.65	0.112	258.0	531.6	4170.8 b	404.6
Tr4	7.17	0.284 b	12.94	0.104	245.0	550.2	3481.8 c	395.2
Tr5	7.17	0.274 b	13.21	0.104	301.5	574.9	2996.3 d	388.8
F-test	ns	*	ns	ns	ns	ns	*	ns
CV	18.53	32.17	16.19	23.25	16.71	8.5	6.28	4.99

Note: Means in a column and a row followed by the same letter are not significantly different, * Significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

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Growth of Chinese kale

1. Plant height

From **Table 38**, the evaluations for efficiency in use of the suspension fertilizers processed by Luxen's Method were compared between the suspension fertilizers applied under drip fertigation and the granule fertilizer applied under broadcasting affecting on plant height of Chinese kale. It was found that at 45 DAT, all of three drip fertigation treatments and broadcasting yield non-significantly different in plant height (22.70-25.82 cm). But they were significantly different in plant height to the plant height of 11.50 cm of the control treatment (Tr_1, unapplied under both drip and broadcasting).

Within 14 DAT, It was noticeable that Tr_5 and Tr_4 yielded the shorter plant height of 8.80 and 9.30 cm than the plant height of 11.14 cm of Tr_2 significantly. The Chinese kale leaves of Tr_5 and Tr_4 showed a little yellow leaves (**Figure 46**). It could be revealed that the fertilizer solution at the rate of 0.049% (total 1764 mg/pot) and 0.098% (total 3528 mg/pot) of 25-7-7 suspension fertilizer for Tr_4 and Tr_5, respectively, were high concentration to them for being firstly applied under drip fertigation. At the same time Tr_3 yielded non-significantly different in the plant height of 10.54 cm to the plant height of 11.14 cm of Tr_2 because of its (Tr_2) fertilizer solutions at the rate of 0.0245% (total 882 mg/pot) 25-7-7 suspension fertilizer being less two times of 0.049% (total 1764 mg/pot) 25-7-7 granule fertilizer and suitable for it. However Tr_5 and Tr_4 were tolerant to those solutions after 14 DAT. At last they were normal plant growth. Tr_2 were applied under broadcasting the 25-7-7 granule fertilizers in the rate of 353 mg/pot/event (total 1764 mg/pot), the total of 5 events. They were tolerant to that rate of use in spite of its concentration of broadcasting was higher than the concentration of drip fertigation. It could be revealed that the broadcasted granular fertilizers were gradually dissolved by 200 ml of watering which affected on low concentration of plant nutrients in root zones.

So the vegetable crops have to be applied under drip fertigation at low rate

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of use when the roots have been developing at induction period.

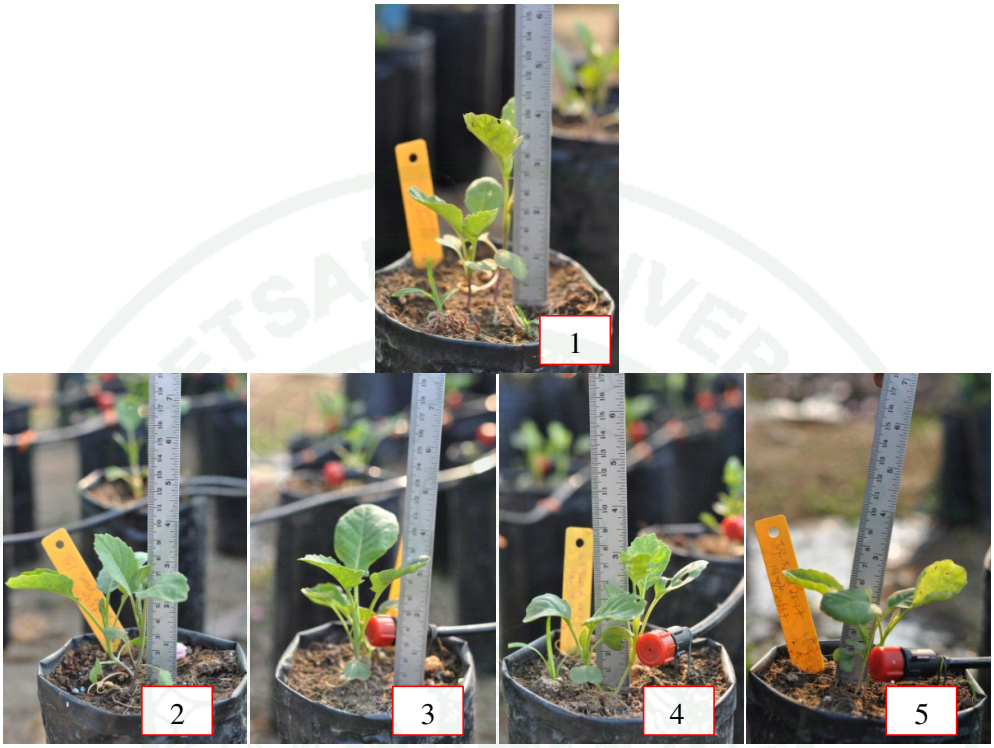

Figure 46 The second fertilizer applications within 14 DAT, effects of fertilizer concentrations on plant growth (leaf color) of Chinese kale, (1) Tr_1 (control) affected on a little yellow leaves, (2) Tr_2 applied under broadcasting 25-7-7 conventional (granular) fertilizer at rate 352 mg/pot/event affected on green leaves, (3) Tr_3 applied under drip fertigation 25-7-7 suspension fertilizer at rate 49 mg/pot/event affected on green leaves, (4) applied under drip fertigation 25-7-7 suspension fertilizer at rate 98 mg/pot/event affected on a little yellow leaves and (5) Tr_5 applied under drip fertigation 25-7-7 suspension fertilizer at rate 196 mg/pot/event affected on a little yellow leaves.

Within 35-42 DAT, all of treatments yielded significantly different in plant height. Tr_2, Tr_3, Tr_4 and Tr_5 yielded non-significantly different in plant height of 22.70-25.82 cm which were significantly different to the plant height of 11.50 cm of

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Tr_1 (**Table 38**). The yields of plant height (22.70-25.82 cm) were related to the plant height of 29.5, 28.1, 24.83 and 18.44 cm in the other researches of Choe *et al.* (2007); Tippawun *et al.* (2012); Chutimon (2010); Khongchai and Yanyong (2010) respectively, which were growth enhancement. Many studies (Osothsapa, 2009; Jones, 1998; MuangThong, 1989) were mentioned that a lack of nitrogen could stunt Chinese kale growth or even caused it to become a dwarf plant. These were related to the plant height of 11.50 cm of Tr_1 that was un-applied under both the granule and the suspension fertilizer.

Both the concentration of 25-7-7 granule and 25-7-7 suspension fertilizer were sufficient plant nutrient for growth enhancement. Tr_2**,** Tr_3**,** Tr_4 and Tr_5 that were applied under broadcasting at the rate of 1764 mg/pot, under drip fertigation of 25-7-7 suspension fertilizer at the rate of 882, 1764 and 3528 mg/pot, respectively, yielded non significantly different in plant height of 22.70-25.82 cm. The rate of 882 mg/pot for Tr_3 were the most appropriate rate of use because of its the least rate of use. This rate was less two times of the granule fertilizer rate of 1764 mg/pot for Tr_2. The rate of 882 mg/pot was equivalent to 23 kg of 25-7-7 suspension fertilizer/rai [based on a density of 108,000 to 220,000 plants/ha, or 26240 plants/rai (Cantwell *et al* .1996)], or total amount of 8.97 kg-Ai./rai (5.75 kg N, 1.61 kg P_2O_5 and 1.61 kg K_2O/rai) which were equivalent to 19.9% of total amount of 45 kg-Ai./rai (20 kg N, 10 kg P_2O_5 and 15 kg K_2O/ rai) in the other research of Tippawun *et al.* (2012). They were related to Pichai (2012); Kusakabe *et al.* (2006) and Thompson *et al.* (2003) who found that the fertigation rate of use was less than amount of 30% the granular fertilizer rate of use.

1. Leaf greenness color at harvest stage

From **Table 38**, the evaluations for efficiency in use of the suspension fertilizers processed by Luxen's Method were compared between the suspension fertilizers applied under drip fertigation and the granule fertilizer applied under broadcasting affecting on leaf greenness. It was noticeable that the increased amounts of suspension fertilizer affected on increasing leaf greenness significantly to Tr_1. While Tr_2 yielded significantly different in leaf greenness to Tr_1.

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Tr_3 yielded significantly different in leaf greenness of 40.62 SPAD unit to the leaf greenness of 48.80 SPAD unit of Tr_2. Tr_4 yielded non-significantly different in leaf greenness of 47.1 SPAD unit to the leaf greenness of Tr_2. Tr_5 yielded non-significantly different in leaf greenness of 53.98 SPAD unit to the leaf greenness of Tr_2. Tr_4 was applied under drip fertigation at the suspension fertilizer rate of 1764 mg/pot that was equal to the granule fertilizer rate of 1764 mg/pot of Tr_2. Tr_5 was two times to the granule fertilizer rate of 1764 mg/pot of Tr_2. Thereby the suspension fertilizers could be applied under drip fertigation instead of the granule fertilizers applied under broadcasting. The leaf greenness in this research was of 40.62-53.98 SPAD unit which were related to the leaf greenness in the other research showed 44.73-58.13 SPAD unit (Supakid and Soraya, 2010).

Table 38 Effects of treatments on plant height of Chinese kale in various Day after transplanting (DAT) and greenness of leaves at harvest time

Treatments	Plant growth					
	Day after transplanting (day)					Leaf greenness (SPAD unit)
	14	21	28	35	45	
	Plant height (cm)					
Tr_1	9.90 abc	10.72	11.36	11.14 b	11.50 B	36.84 z
Tr_2	11.14 a	13.12	15.90	20.84 a	25.82 A	48.80 wx
Tr_3	10.54 ab	14.58	15.60	20.00 a	24.68 A	40.62 yz
Tr_4	9.30 bc	12.96	13.74	19.46 a	22.70 A	47.10 xy
Tr_5	8.80 c	11.80	12.38	17.80 a	23.44 A	53.98 w
F-test	*	ns	ns	*	*	*
C.V.	11.27	17.45	19.91	15.92	16.43	10.91

Note: Means in the column followed by the same letter are not significantly different * Significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

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Yield of Chinese kale

1. Total fresh weight of stem and leaves of Chinese kale

From **Table 39** the evaluations for efficiency in use of the suspension fertilizers processed by Luxen's Method were compared between the suspension fertilizers applied under drip fertigation and the granule fertilizer applied under broadcasting affecting on fresh weight. It was found that all of three drip fertigation treatments yield non-significantly different in fresh weight (27.78**-**28.85 g). But they were significantly different to the fresh weight of 48.74 g of broadcasting treatment (Tr_2). While the control treatment (Tr_1, unapplied under both drip and broadcasting) yielded significantly different to all of treatments in the fresh weight of 3.29 g.

Tr_3, Tr_4 and Tr_5 which yielded non- significantly different in fresh weight of 27.78, 28.85 and 28.23 g respectively were significantly different to Tr_1 and Tr_2 yielded fresh weight of 3.29 and 48.74 g, respectively. It could be revealed that Tr_1 that were not applied under both 25-7-7 granular fertilizer and 25-7-7 suspension fertilizer were lack of plant nutrients, affected on discontinuous plant growth. They were shortened fresh weight of Chinese kale which were related to the studies of Osothsapa (2009); Jones (1998); MuangThong (1989) who mentioned that a lack of nitrogen could stunt Chinese kale growth or even caused it to become a dwarf plant.

Moreover, these were found that Tr_4 and Tr_5 yielded the fresh weight of 28.23-28.85 g, as Tr_2 yielded more amounts of fresh weight of 48.74 g significantly. It could be revealed that the fertilizer solution at rate of 0.049% and 0.098% of 25-7-7 suspension fertilizer for Tr_4 and Tr_5, respectively, were high concentration to them for being firstly applied under drip fertigation (**Figure 46**). They affected on discontinuous plant growth for a time. The impact of high fertilizer concentration in the solutions on yields had been seen at harvest time.

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The yields of Tr_3, Tr_4 and Tr_5 which varied from 27.78-28.85 g fresh weight were less amounts to 39.25and 33.93 g fresh weight of Chinese kale in the other researches of Choe *et al*. (2007); Chutimon (2010), respectively.

It was noticeable that the yields of Tr_3, Tr_4 and Tr_5 which varied from 27.78-28.85 g fresh weight were fewer amounts to 48.74 g fresh weight of Tr_2. These were reviewed that Tr_3, Tr_4 and Tr_5 were dripped by total amounts of 200 ml of water that contained the plant nutrients. They leached from the soil base media in the plastic pots. They affected on shortened nutrient consumption for Tr_3, Tr_4 and Tr_5.

1. Total dried weight of Chinese kale leaf

From **Table 39** all of treatments yielded significantly different in dried weight of Chinese kale. Tr_3, Tr_4 and Tr_5 which yielded non-significantly different in dried weight of 3.28, 3.29 and 3.17 g respectively were significantly different to Tr_1 and Tr2 yielded dried weight of 0.60 and 5.90 g. They were related to the fresh weight described above. The dried weight of 0.60-5.90 g in these research were related to the dried weight of 0.86 and 3.4 g in the other researches of Khongchai and Yanyong (2010)**;** Chutimon (2010).

Nutrient concentrations in Chinese kale leaf

Nitrogen concentration in leaves

From **Table 39,** it was found that the increased amounts of suspension fertilizer affected on increasing nitrogen concentration in leaves of Chinese kale significantly. All of treatments yielded significantly different in nitrogen concentration in leaves to the control treatment (Tr_1). Tr_3 and Tr_2 yielded non-significantly different in nitrogen concentration in leaves (3.70 and 3.22% N). Tr_4, Tr_5 and Tr_2 yielded significantly different in nitrogen concentration in leaves (4.10, 5.01 and 3.22% N).

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Tr_1 yielded the lowest nitrogen concentration in leaves of 1.15% N. At the same time Tr_2 and Tr_3 yielded the nitrogen concentration in leaves of 3.22-3.70% N. Tr_4 yielded the nitrogen concentration in leaves of 4.10% N. Tr_5 yielded the highest nitrogen concentration in leaves of 5.01% N. The 4.5-4.8% N in leaves of Brassica was reported by Maneepong (1994).

It was found that Tr_3 that applied under drip fertigation at the rate of use 882 mg/pot yielded the non-significant different in nitrogen concentration in leaves to Tr_2 that applied under broadcasting granule fertilizer at the rate of use 1764 mg/pot. Thereby, Tr_3 was the appropriate treatment because of its rate of use (882 mg/pot) in a half of the rate of Tr_2 (1764 mg/pot) effecting on non-significant different in nitrogen concentration in leaves.

Phosphorous concentration in leaves

From **Table 39,** it was found that the increased amounts of suspension fertilizer affected on increasing phosphorous concentration in leaves of Chinese kale significantly. All of drip fertigation treatments yielded non-significantly different in phosphorous concentration in leaves (0.34-0.43% P) and yielded significantly different in phosphorous concentration in leaves to the control treatment (Tr_1). Tr_2 yielded non-significantly different in phosphorous concentration in leaves to Tr_1.

Tr_4 and Tr_5 yielded non-significantly different in phosphorous concentration in leaves of 0.40-0.43% P but they were significantly different to Tr_2 (0.29% P). At the same time Tr_3 yielded non-significantly different in phosphorous concentration in leaves of 0.34% P to Tr_2. The 0.8-0.9% P in leaves of Brassica was reported by Maneepong (1994). Thereby Tr_3 that was applied under drip fertigation at rate of use 882 mg/pot was appropriate treatment.

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Potassium concentration in leaves

From **Table 39,** all of treatments yielded non-significantly different in potassium concentration in leaves of 2.81-3.09% K. It was noticeable that the potassium concentration in the leaves was less than the other researches of 3.67 and 5.92% K (Chutimon, 2010; MAFF, 2011). These could be reviewed that all of the soil base media that were tested for this research were contained by greater amounts of exchangeable Ca (4990 mg/pot) (**Table 36**). These affected on inhibiting plant roots to adsorb K nutrient from that soil base media (Direk, 2003).

Table 39 Treatments**,** fresh weight, dried weight and nutrient concentration in leaves of Chinese kale leaves

Treatments	Yields		Nutrients concentration in leaves (% by dried weight)		
	Fresh wt (g)	Dried wt (g)	N	P	K
Tr_1	3.29 c	0.60 c	1.15 d	0.22 c	2.96
Tr_2	48.74 a	5.90 a	3.22 c	0.29 bc	2.88
Tr_3	27.78 b	3.28 b	3.70 bc	0.34 ab	2.81
Tr_4	28.85 b	3.29 b	4.10 b	0.40 a	2.81
Tr_5	28.23 b	3.17 b	5.01 a	0.43 a	3.09
F-test	*	*	*	*	ns
C.V.	53.72	64.42	13.23	24.32	16.08

Note: Means in a column followed by the same letter are not significantly different
* Significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

From Table 40, it was found that Tr_3, Tr_4 and Tr_5 could be applied under drip fertigation instead of broadcasting granule fertilizers (Tr_2) effects on appropriate various plant growth and yields of Chinese kale in that table. It was intended that the

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most appropriate treatment was Tr_3 being used at the rate of 882 mg/pot of 25-7-7 suspension fertilizer that were less two times of 1764 mg/pot of 25-7-7 granule fertilizer. It yielded plant height of 24.68 cm, leaf greenness of 40.62 SPAD unit, fresh weight of 27.78 g, dried weight of 3.28 g, and nutrients concentration in leaves of 3.70% N, 0.34% P and 2.81% K.

Table 40 Comparison of treatments in various plant growth and yields of Chinese Kale for selecting the appropriate treatment instead of Tr_2

Treatments	Plant height (cm)	Leaf greenness (SPAD unit)	Fresh weight (g)	Dried weight (g)	Nutrients concentration in leaves (% by dried weight)		
					N	P	K
Tr_2	25.82 A	48.80 wx	48.74 a	5.90 a	3.22 c	0.29 bc	2.88
Tr3	24.68 A	40.62 yz	27.78 b	3.28 ab	3.70 bc	0.34 ab	2.81
Tr4	22.70 A	47.10 xy	28.85 b	3.29 ab	4.10 b	0.40 a	2.81
Tr5	23.44 A	53.98 w	28.23 b	3.17 ab	5.01 a	0.43 a	3.09
F-test	*	*	*	*	*	*	ns
C.V.	16.43	10.91	53.72	64.42	13.23	24.32	16.08

Note: Means in a column followed by the same letter are not significantly different * Significantly different, ns = non-significantly different, according to LSD ($p \leq 0.05$)

The fertilizer cost rates of use between suspension fertilizer and granule fertilizer

The suspension fertilizer's costs (1851.20 Baht/rai) were compared to the granule fertilizer's costs (1008.90 Baht/rai) showed that they were greater than the granule fertilizer's costs (Table 41). It was noticeable that the suspension rates of use were 50% of the granule fertilizer rates in this research. However, the suspension fertilizer rates of use were usually less than amount of 30% the granule fertilizer rates of use. This experiment was aimed to investigate efficiency in use by comparing between the granule and the suspension fertilizer mainly. It would be thoroughly

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designed to experiments for obtaining a result in accuracy of the rate of use for calculation in fertilizer costs. Pichai (2012) found that the suspension rate of use in Mandarin orange orchard in Chiang Mai province was 17% of granular fertilizer rate of use while the recommendation less than amount of 30% for other countries (Kusakabe *et al*., 2006; Thompson *et al*., 2003).

Table 41 Comparison in fertilizer cost between the suspension and the granule

	The suspension fertilizer cost	The granule fertilizer cost
Unit price[1/] (Baht/kg)	80	21.80
Rate of use[2/] (kg/rai)	23.14	46.28
Total cost	1851.20	1008.90

Note: [1/] available price in January, 2014

[2/] the rates of use derived from this research (882 and 1764 mg/pot)

25-7-7 analysis grade of suspension fertilizer processed by Luxen's method could be applied under drip fertigation at the rate of 50% of the granule fertilizer rate of use or 19.9% of the granule rate (equivalent to active ingredient) of use in Chinese kale yielding plant height of 24.68 cm, leaf greenness of 40.62 SPAD unit, fresh weight of 27.78 g, dried weight of 3.28 g, and nutrients concentration in leaves of 3.70% N, 0.34% P and 2.81% K.

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CONCLUSION AND RECOMMENDATION

Conclusion

From experiment 1-5, the present suspension fertilizer production method by using solid raw materials instead of liquid ones was Luxen's method. It was consisted of as following: 1) to divide total weight of raw materials into 2 portions, the one for clear liquid mixed solution stage and the another for suspended liquid, 2) milled solid raw materials in particle size of >20 meshes, 3) 1820 rpm speed of agitator for clear liquid mixed solution stage and 2620 rpm speed of agitator for suspended liquid, 4) the temperature of solution: 30-40°C, 5) the suspending agent: xanthan gum. This Luxen's method could be processed in various suspension fertilizer grades such as in high N, high P_2O_5, high K_2O, and equal NPK nutrient ratio with their appropriate chemical and physical properties. They could be stored for a long period at 180 day in normal room temperature. Moreover, the 25-7-7 suspension fertilizer processed by Luxen's method could be applied under drip fertigation at the rate of 50% of the granule fertilizer rate of use or 19.9% of the granule rate (equivalent to active ingredient) of use in Chinese kale yielding appropriateness in plant growth and yields.

Recommendation

1) In cast of the pour-ability yielding more amounts of 5% remaining product, it was recommended to decrease amounts of suspending agent for adjusting the appropriate viscosity.

2) Removing the exchangeable calcium in soil before planting

3) Be carefully adequate watering for protecting the leaching

4) The vegetable crops have to be applied under drip fertigation at low suspension fertilizer rate of use when the roots have been developing at induction period.

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APPENDIX

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Appendix Table 1 Effects of speeds of agitator and particle size of solid raw materials on the dissolving time for urea 1 dissolved completely

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Mesh	1	118.148	118.148	1165.763	< 2.2e-16***
Speed	2	9.618	4.809	47.448	6.658e-08***
Mesh: Speed	2	4.112	2.056	20.286	2.445e-05***
Residuals	18	1.824	0.101		
qf(0.05,2,18,lower.tail=F) 3.554557					
C.V. (%)			9.47		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 2 Effects of speeds of agitator and particle size of solid raw materials on the dissolving time for xanthan gum dissolved completely

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Mesh	1	0.002	0.002	0.5352	0.4738
Speed	2	130.983	65.491	21032.0219	<2e-16 ***
Mesh: Speed	2	0.0003083	0.0001542	0.0495	0.9518
Residuals	18	0.056	0.003		
qf(0.05,2,18,lower.tail=F) 3.554557					
C.V. (%)			1.61		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 3 Effects of suspending agent and temperatures of solution on pH of 25-7-7 analysis grade of suspension fertilizer in experiment 2

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
temp	1	0.093750	0.093750	7.7586	0.01221 *
gum	2	0.085833	0.042917	3.5517	0.05010
temp:gum	2	0.022500	0.011250	0.9310	0.41232
Residuals	18	0.217500	0.012083		
qf(0.05,2,18,lower.tail=F) 3.554557					
C.V. (%)			1.95		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 4 Effects of suspending agent and temperatures of solution on specific gravity of 25-7-7 analysis grade of suspension fertilizer in experiment 2

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
temp	1	0.0001602	0.0001602	0.2250	0.6409
gum	2	0.0039056	0.0019528	2.7436	0.0912
temp:gum	2	0.0034926	0.0017463	2.4535	0.1142
Residuals	18	0.0128115	0.0007118		
qf(0.05,2,18,lower.tail=F) 3.554557					
C.V. (%)			2.18		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 5 Effects of suspending agent and temperatures of solution on viscosity of 25-7-7 analysis grade of suspension fertilizer in experiment 2

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
temp	1	20174001	20174001	58.922	4.393e-07 ***
gum	2	114966946	57483473	167.891	2.285e-12 ***
temp:gum	2	11614981	5807491	16.962	7.230e-05 ***
Residuals	18	6162935	342385		
qf(0.05,2,18,lower.tail=F) 3.554557					
C.V. (%)			13.84		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 6 Effects of suspending agent and temperatures of solution on stability of 25-7-7 analysis grade of suspension fertilizer in experiment 2

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
temp	1	3.2420e-28	3.2420e-28	1	0.3306
gum	2	6.4850e-28	3.2420e-28	1	0.3874
temp:gum	2	6.4850e-28	3.2420e-28	1	0.3874
Residuals	18	5.8362e-27	3.2420e-28		
qf(0.05,2,18,lower.tail=F) 3.554557					
C.V. (%)			1.80		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 7 Effects of suspending agent and temperatures of solution on pour-ability of 25-7-7 analysis grade of suspension fertilizer in experiment 2

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
temp	1	27.735	27.735	10.1264	0.00516 **
gum	2	131.582	65.791	24.0211	8.3e-06 ***
temp:gum	2	20.747	10.374	3.7876	0.04237 *
Residuals	18	49.300	2.739		
qf(0.05,2,18,lower.tail=F) 3.554557					
C.V. (%)			26.37		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 8 Effects of stored periods on pH of 25-7-7 analysis grade of suspension fertilizer in experiment 3

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
trt	5	0.022083	0.004417	0.2727	0.9210
rep	3	0.014583	0.004861	0.3002	0.8248
Residuals	15	0.242917	0.016194		
qf(0.05,5,15,lower.tail=F) 2.901295					
C.V. (%)			2.29		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 9 Effects of stored periods on specific gravity of 25-7-7 analysis grade of suspension fertilizer in experiment 3

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
trt	5	0.0018052	0.0003610	1.7063	0.1938
rep	3	0.0008648	0.0002883	1.3623	0.2922
Residuals	15	0.0031740	0.0002116		
qf(0.05,5,15,lower.tail=F) 2.901295					
C.V. (%)			1.15		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 10 Effects of stored periods on viscosity of 25-7-7 analysis grade of suspension fertilizer in experiment 3

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
trt	5	975446316	195089263	1081.4707	<2e-16 ***
rep	3	214355	71452	0.3961	0.7577
Residuals	15	2705888	180393		
qf(0.05,5,15,lower.tail=F) 2.901295					
C.V. (%)			6.23		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 11 Effects of stored periods on stability of 25-7-7 analysis grade of suspension fertilizer in experiment 3

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
trt	5	9.4039	1.8808	178.2173	8.342e-13 ***
rep	3	0.0114	0.0038	0.3585	0.7838
Residuals	15	0.1583	0.0106		
qf(0.05,5,15,lower.tail=F) 2.901295					
C.V. (%)			0.10		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 12 Effects of stored periods on pour-ability of 25-7-7 analysis grade of suspension fertilizer in experiment 3

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
trt	5	11.0771	2.2154	12.4495	6.732e-05 ***
rep	3	1.0646	0.3549	1.9941	0.1582
Residuals	15	2.6693	0.1780		
qf(0.05,5,15,lower.tail=F) 2.901295					
C.V. (%)			10.22		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 13 Effects of fertilizer grade and stored periods on N concentration in its suspension fertilizer after having been stored at 180 d in experiment 4

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
trt	5	782.28	156.46	7173.9962	<2e-16 ***
rep	1	0.04	0.04	1.6851	0.2116
Residuals	17	0.2116	0.02		
qf(0.05,5,17,lower.tail=F) 2.809996					
C.V. (%)			0.91		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 14 Effects of fertilizer grade and stored periods on P_2O_5 concentration in its suspension fertilizer after having been stored at 180 d in experiment 4

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
trt	5	851.00	170.20	4346.0950	<2e-16 ***
rep	1	0.01	0.01	0.1724	0.6832
Residuals	17	0.67	0.04		
qf(0.05,5,17,lower.tail=F) 2.809996					
C.V. (%)			1.32		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 15 Effects of fertilizer grade and stored periods on K_2O concentration in its suspension fertilizer after having been stored at 180 d in experiment 4

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
trt	5	654.29	130.86	9739.2138	<2e-16 ***
rep	1	0.01	0.01	1.0482	0.3203
Residuals	17	0.23	0.01		
qf(0.05,5,17,lower.tail=F) 2.809996					
C.V. (%)			0.69		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 16 Effects of fertilizer grade and stored periods on pH of their suspension fertilizers after having been stored at various periods in experiment 4

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
grade	5	6.2496	1.2499	230.7538	<2e-16 ***
day	3	0.0013	0.0004	0.0769	0.9723
Grade:day	15	0.0888	0.0059	1.0923	0.3789
Residuals	72	0.3900	0.0054		
qf(0.05,15,72,lower.tail=F) 1.807571					
C.V. (%)			1.39		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 17 Effects of fertilizer grade and stored periods on specific gravity of their suspension fertilizers after having been stored at various periods in experiment 4

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
grade	5	0.45557	0.09111	1189.6251	<2e-16 ***
day	3	0.00016	0.00005	0.6789	0.5678
Grade:day	15	0.00064	0.00004	0.5542	0.8994
Residuals	72	0.00551	0.00008		
qf(0.05,15,72,lower.tail=F) 1.807571					
C.V. (%)			0.65		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 18 Effects of fertilizer grade and stored periods on viscosity of their suspension fertilizers after having been stored at various periods in experiment 4

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
grade	5	415782976	83156595	23.7744	4.925e-14 ***
day	3	2201418694	733806231	209.7945	< 2.2e-16 ***
Grade:day	15	212527529	14168502	4.0508	2.781e-05 ***
Residuals	72	251837147	3497738		
qf(0.05,15,72,lower.tail=F) 1.807571					
C.V. (%)			27.90		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 19 Effects of fertilizer grade and stored periods on stability of their suspension fertilizers after having been stored at various periods in experiment 4

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
grade	5	0.3650	0.0730	1.1838	0.3257
day	3	2.2050	0.7350	11.9189	2.009e-06 ***
Grade:day	15	1.0950	0.0730	1.1838	0.3040
Residuals	72	4.4400	0.0617		
qf(0.05,15,72,lower.tail=F) 1.807571					
C.V. (%)			0.24		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 20 Effects of fertilizer grade and stored periods on pour-ability of their suspension fertilizers after having been stored at various periods in experiment 4

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
grade	5	22.981	4.596	14.3765	9.422e-10 ***
day	3	80.832	26.944	84.2770	< 2.2e-16 ***
Grade:day	15	36.278	2.419	7.5648	9.762e-10 ***
Residuals	72	23.019	0.320		
qf(0.05,15,72,lower.tail=F) 1.807571					
C.V. (%)			18.32		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 21 Effects of fertilizer grade and stored periods on salting out of their suspension fertilizers after having been stored at various periods in experiment 4

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
grade	5	0.21675	0.04335	55.145	< 2.2e-16 ***
day	3	0.13005	0.04335	55.145	< 2.2e-16 ***
Grade:day	15	0.65025	0.04335	55.145	< 2.2e-16 ***
Residuals	72	0.05660	0.00079		
qf(0.05,15,72,lower.tail=F) 1.807571					
C.V. (%)			132.26		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 22 Effects of treatments on pH of soil base media after tested in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	0.446	0.446	0.2350	0.6334
trt	4	5.109	1.277	0.6735	0.6185
Residuals	19	36.031	1.896		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			18.53		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 23 Effects of treatments on electrical conductivity of soil base media after tested in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	0.000242	0.000242	0.0230	0.88106
trt	4	0.175704	0.043926	4.1747	0.01361 *
Residuals	19	0.199918	0.010522		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			32.17		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 24 Effects of treatments on organic matter of soil base media after tested in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	0.112	0.112	0.0270	0.8713
trt	4	9.270	2.317	0.5567	0.6967
Residuals	19	79.100	4.163		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			16.19		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 25 Effects of treatments on total % N of soil base media after tested in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	0.0008820	0.0008820	1.1325	0.30059
trt	4	0.0083200	0.0020800	2.6706	0.06379
Residuals	19	0.0147980	0.0007788		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			23.25		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 26 Effects of treatments on available P of soil base media after tested in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	1013	1013	0.4541	0.5085
trt	4	16883	4221	1.8928	0.1532
Residuals	19	42368	2230		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			16.71		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 27 Effects of treatments on exchangeable K of soil base media after tested in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	46	46	0.0194	0.8908
trt	4	21227	5307	2.2528	0.1015
Residuals	19	44756	2356		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			8.51		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 28 Effects of treatments on exchangeable Ca of soil base media after tested in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	6464	6464	0.097	0.7588
trt	4	15242760	3810690	57.199	.479e-10 ***
Residuals	19	1265805	66621		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			6.28		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 29 Effects of treatments on exchangeable Mg of soil base media after tested in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	591.7	591.7	1.4548	0.2426
trt	4	3385.6	846.4	2.0811	0.1234
Residuals	19	7727.4	406.7		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			4.99		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 30 Effects of treatments on plant height of Chinese kale in 14 DAT in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	1.1858	1.1858	0.9451	0.3432
trt	4	17.5536	4.3884	3.4977	0.0266*
Residuals	19	23.8382	1.2546		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			11.27		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 31 Effects of treatments on plant height of Chinese kale in 21 DAT in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	7.762	7.762	1.5958	0.2218
trt	4	42.442	10.610	2.1815	0.1101
Residuals	19	92.414	4.864		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			17.45		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 32 Effects of treatments on plant height of Chinese kale in 28 DAT in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	29.032	29.032	3.8467	0.06467
trt	4	78.118	19.529	2.5876	0.06988
Residuals	19	143.400	7.547		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			19.91		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 33 Effects of treatments on plant height of Chinese kale in 35 DAT in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	15.792	15.792	1.9547	0.1781917
trt	4	305.906	76.477	9.4659	0.0002198 ***
Residuals	19	153.504	8.079		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			15.92		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 34 Effects of treatments on plant height of Chinese kale in 45 DAT in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	37.32	37.32	2.9543	0.1019
trt	4	669.48	167.37	13.2478	2.551e-05 ***
Residuals	19	240.04	12.63		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			16.43		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 35 Effects of treatments on leaf greenness of Chinese kale leaves at harvest time in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	6.55	6.55	0.2660	0.6119930
trt	4	920.83	230.21	9.3449	0.0002375 ***
Residuals	19	468.06	24.63		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			10.91		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 36 Effects of treatments on fresh weight of Chinese kale at harvest time in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	15.9	15.9	0.0737	0.788949
trt	4	5198.2	1299.5	6.0092	0.002669 **
Residuals	19	4108.9	216.3		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			53.72		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 37 Effects of treatments on dried weight of Chinese kale at harvest time in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	0.195	0.195	0.0445	0.83520
trt	4	70.329	17.582	4.0172	0.01585 *
Residuals	19	83.157	4.377		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			64.42		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 38 Effects of treatments on N concentration in Chinese kale leaves in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	0.062	0.062	0.2999	0.5903
trt	4	41.322	10.331	50.0137	7.918e-10 ***
Residuals	19	3.925	0.207		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			13.23		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Table 39 Effects of treatments on P concentration in Chinese kale leaves in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	0.007688	0.007688	1.1349	0.300089
trt	4	0.146536	0.036634	5.4078	0.004429 **
Residuals	19	0.128712	0.006774		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			24.32		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Appendix Table 40 Effects of treatments on K concentration in Chinese kale leaves in experiment 5

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
rep	1	0.2152	0.2152	0.9824	0.3341
trt	4	0.2877	0.0719	0.3284	0.8554
Residuals	19	4.1616	0.2190		
qf(0.05,4,19,lower.tail=F) 2.895107					
C.V. (%)			16.08		

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

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Appendix Figure 1 Agitator with adjustable speed for agitating the suspension in homogenize.



Appendix Figure 2 Disc mill for milling the solid raw materials in particle size of >20 meshes

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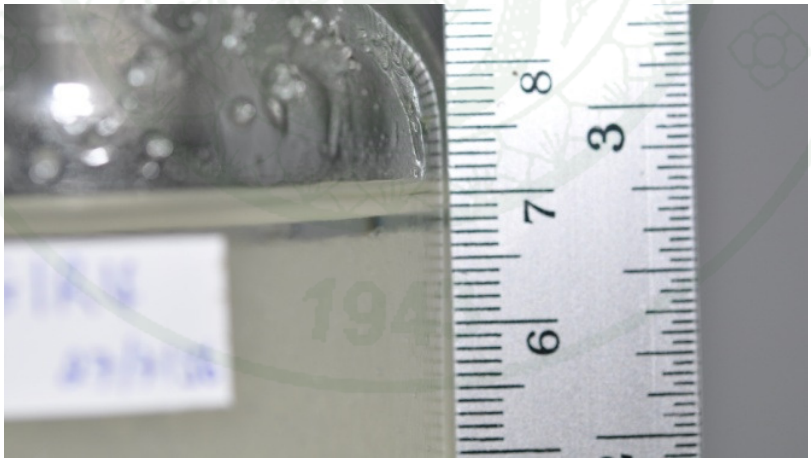
Appendix Figure 3 A Brookfield viscometer, digital viscometer NDJ 5S type from China. It was used for evaluation in viscosity of the suspension fertilizers.



Appendix Figure 4 The supernatants were measured by the scale for determination of stability after the suspensions had been stored at various periods.

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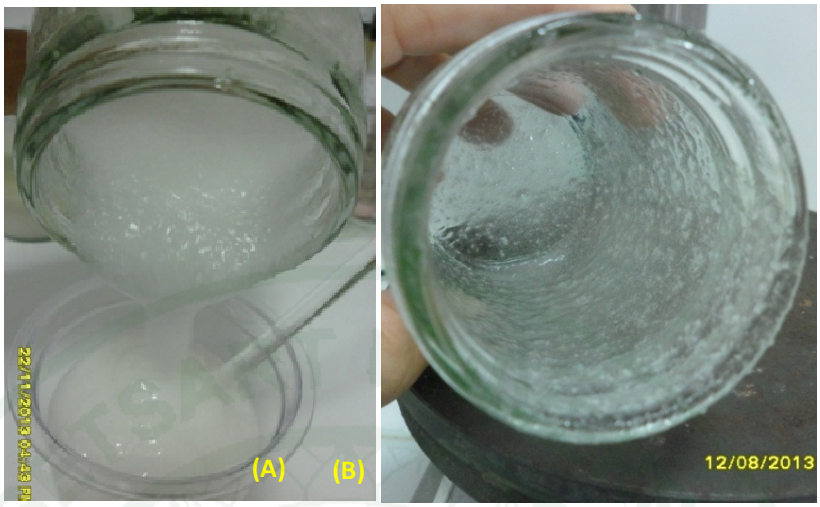

Appendix Figure 5 Pour-ability determination, (A) The suspension had been pouring for receiving the poured products, (B) After that, the remaining products stuck on the wall of container.



Appendix Figure 6 Salting out determination, the suspensions were sieved through the eight inch diameter with 20 mesh screen test sieve. The retained crystals were washed with acetone mixture, dried and weighed for determination of % retained crystals.

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Appendix Figure 7 Portable pH meter: Checker® from USA, for detecting the pH of the suspensions



Appendix Figure 8 Specific gravity hydrometer, for detecting the specific gravity of the suspensions



Appendix Figure 9 Minolta Chlorophyll Meter: SPAD-502, Japan, for evaluation in leaf greenness of Chinese kale leaves

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Appendix Figure 10 Protein / nitrogen determinator (LECO, FP-528, Miami, USA), for detecting % N in Chinese kale leaves



Appendix Figure 11 Spectrophotometer (Milton Roy: Spectonic Genesys 5, USA), for detecting the % P in Chinese kale leaves

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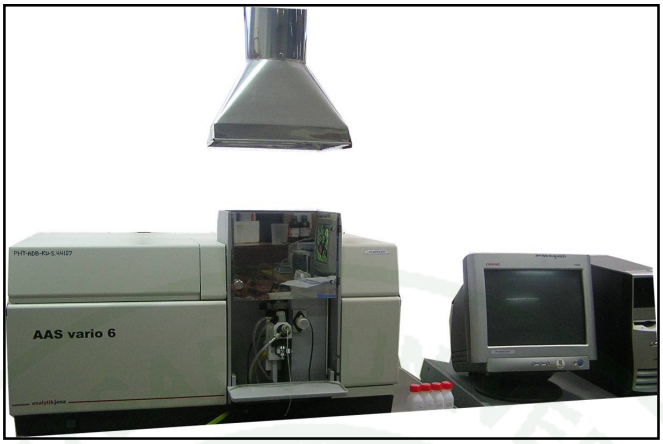

Appendix Figure 12 Atomic Absorption Spectrophotometer (Analytic Jena, vario 6, Jena, Germany), for detecting the % K in Chinese kale leaves



Appendix Figure 13 The clear Liquid layer appeared on bottom of solution occurred when the suspension were lower density than density of the clear liquid.

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Appendix Figure 14 Formation of needle crystals of urea 1, they formed in crystals at the top and the bottom of the solution and then they lumped together for long crystals.



Appendix Figure 15 The retained crystals would occur when the suspensions were consisted of insufficient suspending agent, the non-dissolved solid raw materials formed in salting out.

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Appendix Figure 16 The suspensions were consisted of original size of urea 1.They were un-appropriate because they affected on clogging of emitter.



Appendix Figure 17 The suspensions were consisted of >20 meshes size of urea1. They were appropriate suspensions.

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(Tr_1) (Tr_2) (Tr_3) (Tr_4) (Tr_5)

Appendix Figure 18 The drip fertigation system: (A) fertilizer solution tanks, (B) micro tubes carried the fertilizer solutions to the Chinese kale in the pots



Appendix Figure 19 Drip emitter with adjustable volume

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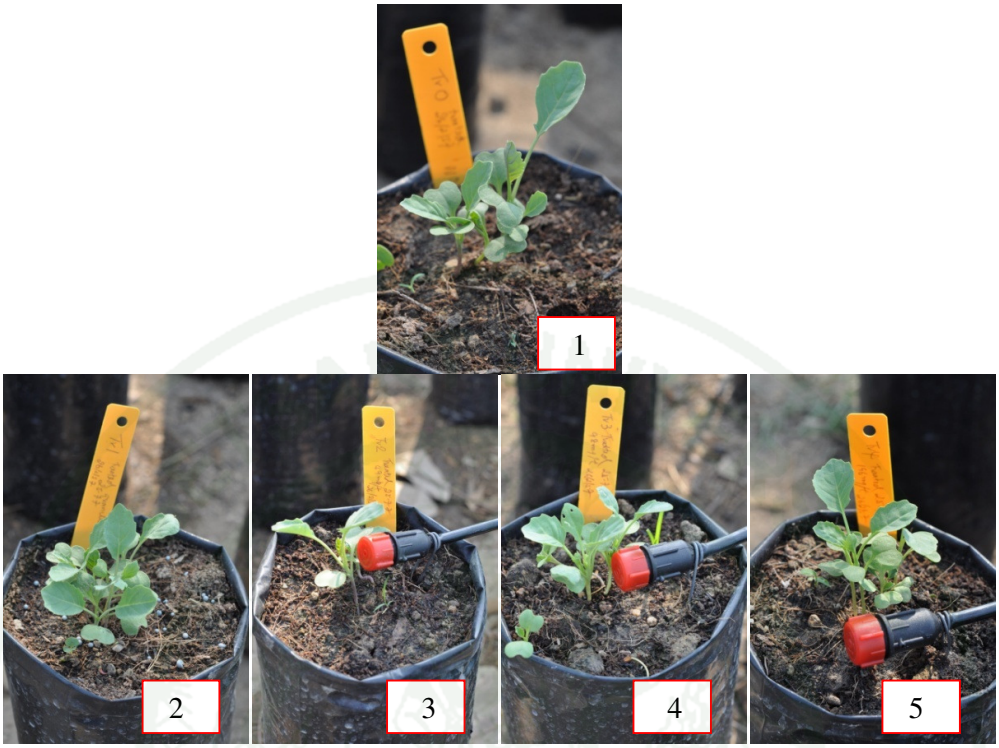

Appendix Figure 20 Comparison between granule fertilizer application and suspension fertilizer application at 7 DAT on leaves growth of Chinese kale: (1) Tr_1 (control) effected on green leaves, (2) Tr_2 applied under broadcasting 25-7-7 conventional (granular) fertilizer at rate 352 mg/pot/event effected on green leaves, (3) Tr_3 applied under drip fertigation 25-7-7 suspension fertilizer at rate 49 mg/pot/event effected on green leaves, (4) applied under drip fertigation 25-7-7 suspension fertilizer at rate 98 mg/pot/event effected on green leaves and (5) Tr_5 applied under drip fertigation 25-7-7 suspension fertilizer at rate 196 mg/pot/event effected on green leaves.

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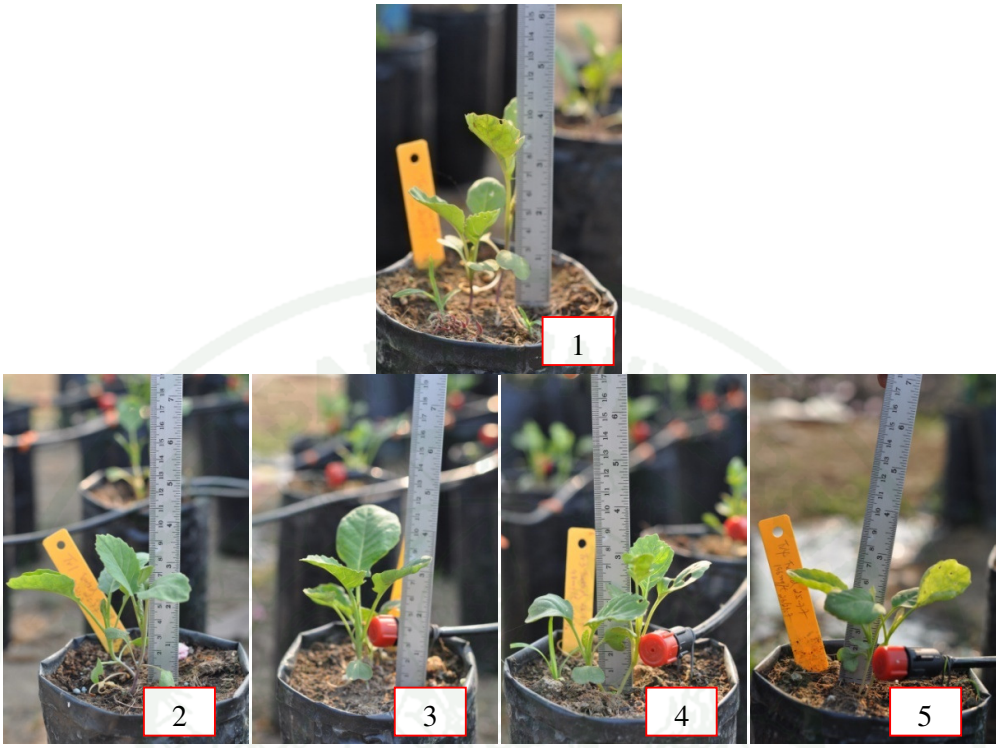

Appendix Figure 21 Comparison between granule fertilizer application and suspension fertilizer application at 14 DAT on leaves growth of Chinese kale: (1) Tr_1 (control) effected on a little yellow leaves, (2) Tr_2 applied under broadcasting 25-7-7 conventional (granular) fertilizer at rate 352 mg/pot/event effected on green leaves, (3) Tr_3 applied under drip fertigation 25-7-7 suspension fertilizer at rate 49 mg/pot/event effected on green leaves, (4) applied under drip fertigation 25-7-7 suspension fertilizer at rate 98 mg/pot/event effected on a little yellow leaves and (5) Tr_5 applied under drip fertigation 25-7-7 suspension fertilizer at rate 196 mg/pot/event effected on a little yellow leaves.

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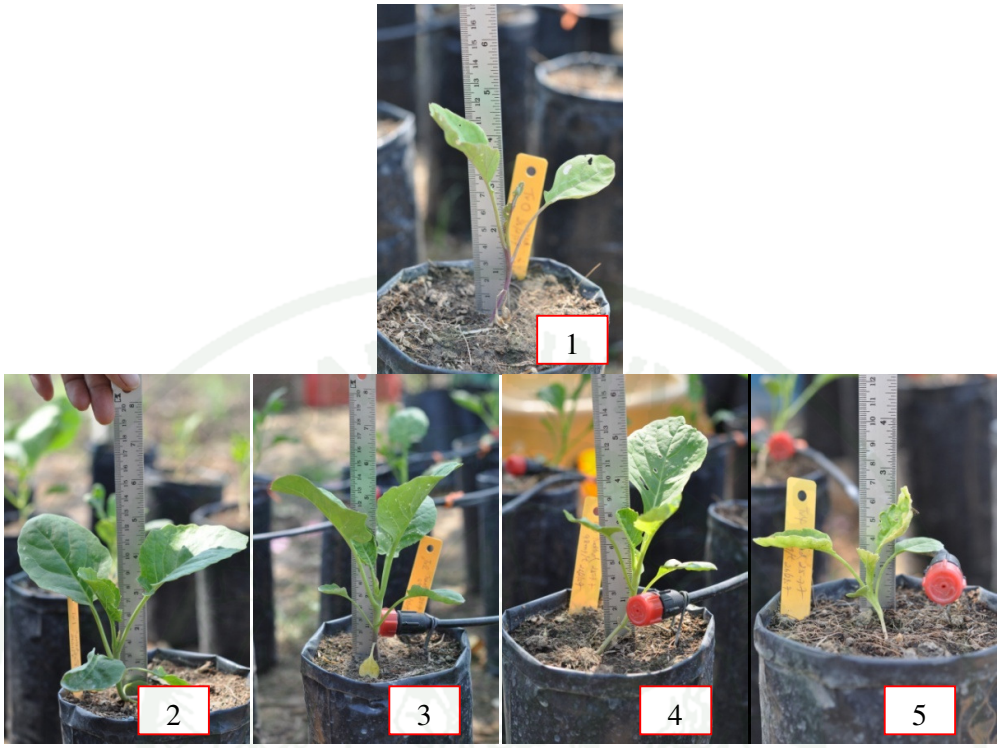

Appendix Figure 22 Comparison between granule fertilizer application and suspension fertilizer application at 21 DAT on leaves growth of Chinese kale: (1) Tr_1 (control) effected on a little yellow leaves, (2) Tr_2 applied under broadcasting 25-7-7 conventional (granular) fertilizer at rate 352 mg/pot/event effected on green leaves, (3) Tr_3 applied under drip fertigation 25-7-7 suspension fertilizer at rate 49 mg/pot/event effected on green leaves, (4) applied under drip fertigation 25-7-7 suspension fertilizer at rate 98 mg/pot/event effected on a little yellow leaves and (5) Tr_5 applied under drip fertigation 25-7-7 suspension fertilizer at rate 196 mg/pot/event effected on a little yellow leaves.

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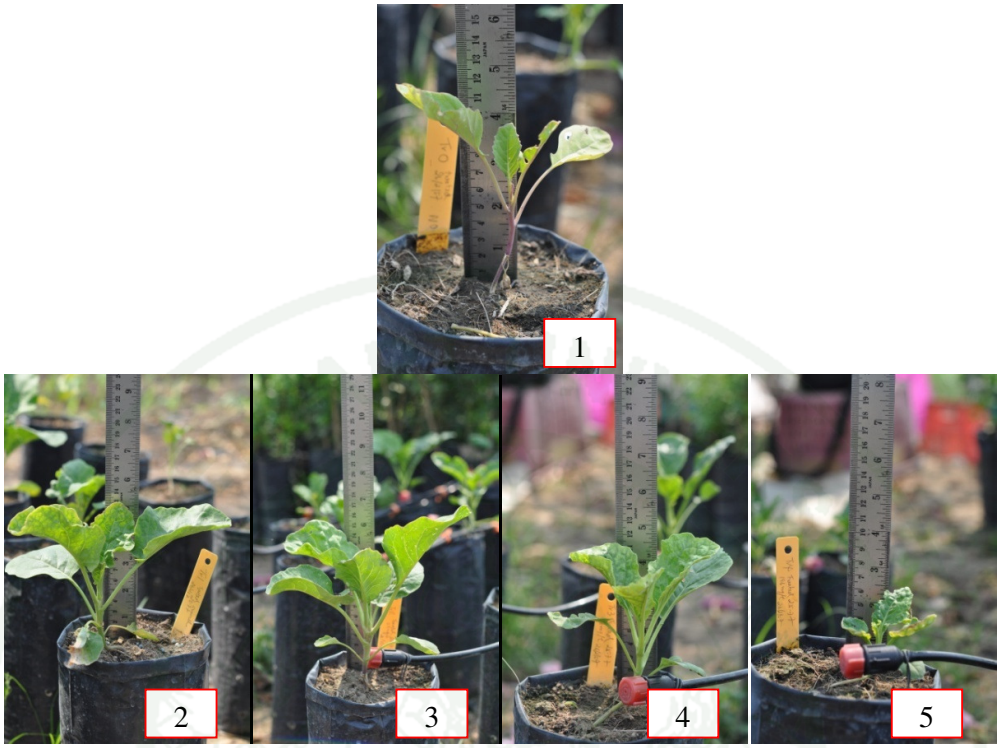

Appendix Figure 23 Comparison between granule fertilizer application and suspension fertilizer application at 28 DAT on leaves growth of Chinese kale: (1) Tr_1 (control) effected on a little yellow leaves, (2) Tr_2 applied under broadcasting 25-7-7 conventional (granular) fertilizer at rate 352 mg/pot/event effected on green leaves, (3) Tr_3 applied under drip fertigation 25-7-7 suspension fertilizer at rate 49 mg/pot/event effected on green leaves, (4) applied under drip fertigation 25-7-7 suspension fertilizer at rate 98 mg/pot/event effected on a little yellow leaves and (5) Tr_5 applied under drip fertigation 25-7-7 suspension fertilizer at rate 196 mg/pot/event effected on yellow leaves and stunt.

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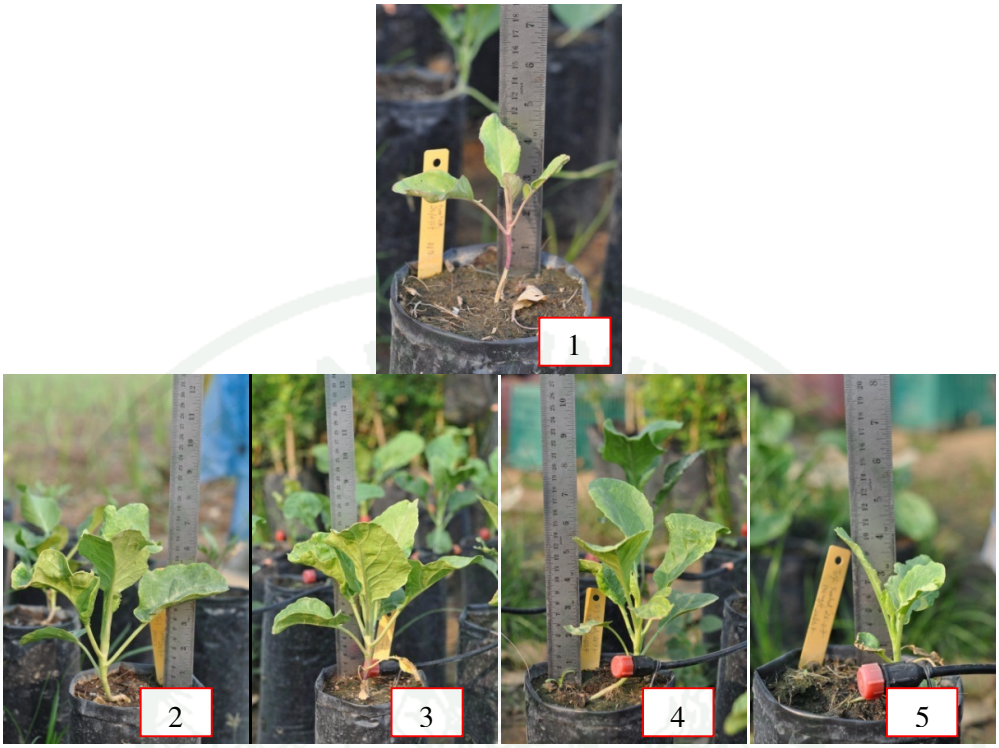

Appendix Figure 24 Comparison between granule fertilizer application and suspension fertilizer application at 35 DAT on leaves growth of Chinese kale: (1) Tr_1 (control) effected on a little yellow leaves, (2) Tr_2 applied under broadcasting 25-7-7 conventional (granular) fertilizer at rate 352 mg/pot/event effected on green leaves, (3) Tr_3 applied under drip fertigation 25-7-7 suspension fertilizer at rate 49 mg/pot/event effected on green leaves, (4) applied under drip fertigation 25-7-7 suspension fertilizer at rate 98 mg/pot/event effected on green leaves and (5) Tr_5 applied under drip fertigation 25-7-7 suspension fertilizer at rate 196 mg/pot/event effected on yellow leaves.

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Appendix Figure 25 Comparison between granule fertilizer application and suspension fertilizer application at harvest time 42 DAT on leaves growth of Chinese kale: (1) Tr_1 (control) effected on a little yellow leaves, (2) Tr_2 applied under broadcasting 25-7-7 conventional (granular) fertilizer at rate 352 mg/pot/event effected on green leaves, (3) Tr_3 applied under drip fertigation 25-7-7 suspension fertilizer at rate 49 mg/pot/event effected on green leaves, (4) applied under drip fertigation 25-7-7 suspension fertilizer at rate 98 mg/pot/event effected on green leaves and (5) Tr_5 applied under drip fertigation 25-7-7 suspension fertilizer at rate 196 mg/pot/event effected on a little yellow leaves.

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