Co-operative Education Report

Phthalate and Adipate esters in

Love Starches (Thailand) Limited' s bag

By

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this report is the part of subject 502 321 (Co-operative Education)

Food Technology

Agriculture Technology Institute, Suranaree University of Technology

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Love Starches (Thailand) Limited' s bag

By

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worked at

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Acknowledgment

I have a good work experiences between training and working in Love Starches (Thailand) Limited since 12th January to 30 April 1999. Thank you for warm friendship from everybody and thank you for:

Ministry of Public Health and Suranaree University of Technology that gave me many knowledge.

Mr. Alan Colwell, the director of Love Starches (Thailand) Limited that gave me an opportunity to training in the company.

Mr. Warwick Gibbons, sale & technical manager that checked and gave me suggestion about the report.

Ms. Wanna Chungprasert, administration officer that suggested me an idea to go to the Ministry of Public Health

Roongfa La-khumlek

April 1999

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The analysis of phthalates and adipates esters in Love Starches (Thailand) Limited' s multiwall paper bag with and without plastic line showed presence of phthalates with the most concentration in the plastic lined paper bag. The total phthalates in paper bags without plastic line (12 mg/kg) are not over the limit but total phthalates in paper bag with plastic line (33 mg/kg) is over the limit of Love Starches (Thailand) Limited (15 mg/kg) and adipates were not detected in any of the samples analysed.

Summary

Phthalates and adipates are used as plasticizers in plastic, printing ink and adhesives. The previous studies showed that they can migrate into the food and can cause many risk to the human for example can lead to carcinogens and weak estrogen activity, so their use must be strictly controled.

George Weston Foods, the parent to Love Starches (Thailand) Limited has set the limit of 15 mg/kg phthalates and adipates in packaging materials.

The bag of Love Starches (Thailand) Limited, they are multiwall paper bags with printing. They were sent to Australian Food Industry Science Centre for evaluate for phthalates and adipates. The results showed that there are 33 mg/kg in the bag with plastic liner and 12 mg/kg in the bag without plastic liner that use to pack Maltodextrin and Dextrose in Indonesia these products are not manufactured by Love Starches (Thailand) Limited and no adipates were detected in any of the samples.

Further work is required to reduce phthalates and adipates levels into George Weston Foods limit while the plastic liner still requires. To this end, the bag supplier(Kadard Rungrogn Company Limited) to Love Starches (Thailand) Limited has been informed the results and request letter for a guarantee that they will not use phthalates and adipates an the manufacture of packaging materials for Love Starches (Thailand) Limited.

Introduction

A Plasticizers is a chemical agent which is added into a material (plastic, resin or elastomer) to make them softer and more flexible. The majority of plasticizer are esters of phthalic acid esters (phthalates); next importance are those based on adipic acid(Robertson, 1993).

Primary plasticizers can be employed as the sole plasticizing ingredient in plastic. They demonstrate a high degree of efficiency (the ability to impart flexibility per unit weight) a permanence(The Staff of Modern Plastics Magazine, 1994).

o-phthalate-benzenedicarboxylates led by di(2-ethylhexyl)phthalates (DOP or DEHP) are the preeminent family of primary plasticizers for use in PVC and other plastics.

Secondary plasticizers comprise a class of additives that contribute to flexibility but cannot; on their own satisfy basic plasticizer requirement. Petroleum derivatives are added for cost reduction and consist of aliphatic, aromatic or chlorinated hydrocarbon(The Staff of Modern Plastics Magazine, 1994)

Phthalates are a group of organic chemical prepared from the esterification of phthalic acid are by far the most important class and probably constitute about 75% of plasticizer used (Brydson, 1969)phthalates occur naturally in coal, crude oil and shale and are used as plasticizers in a wide range of household and consumer goods, use in lubricating oils and use as carriers for perfume in cosmetics. The use of phthalates in plastic food packaging is limited for example to the manufacture of some adhesives and some printing inks. Phthalates are no longer used in the manufacture of cling film and most other food contact plastic material but it was found in Love Starches (Thailand) Limited plastic liner.

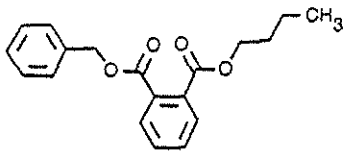
Phthalic acid esters, di-2-ethylhexyl phthalate(DEHP) is the most widely used. DEHP is demonstrated carcinogen in rats and mice, the implications to humans have yet to be determined (Robertson, 1993)

Phthalic acid esters(PAEs) are widely used as plasticizers in the production of plastics (particularly PVC), as well as printing inks to improve the adhesion, flexibility and resistance of printing. Di-2-ethylhexyl phthalate(DEHP), dibutyl phthalate(DBP), butylbezyl phthalate(BBP), diethyl phthalate(DEP) and dicyclohexyl phthalate(DCHP) are most frequently used as the plasticizers. Phthalates are not bound chemically in the plastics and can consequently penetrate the materials, be leached into liquid environments and migrate from the other printed side through the material into the food.

The structure of phthalates commonly used as plasticizers.

1).Benzyl butyl phthalate

-BBP, phthalic acid benzyl butyl ester.



picture 1: the structure of benzyl butyl phthalate(BBP)

-$C_{19}H_{20}O_4$

-Molecular weight = 312.37 g/mol

-1 L = 1.2 kg

-Melting range (-45) - (-35 °C)

-Boiling range/13 hPa 235-255 °C

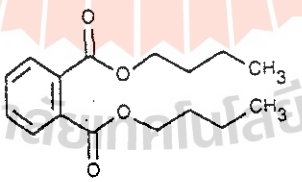
-Immiscible with water

-Explosive limit 1.2 by vol%

-Ignition temperature 435 °C

2).Dibutyl phthalates

-DBP, phthalic acid dibutyl ester



picture 2: the structure of dibutyl phthalate(DBP)

-$C_{16}H_{22}O_4$

-Molecular weight = 278.35 g/mol

-1 L = 1.05 kg

-Melting point -35 °C

-Boiling point 340 °C

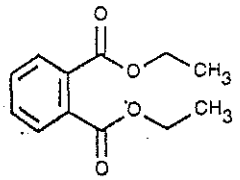
-Solub. in water/20 °C 0.4 g/l

-Ignition temperature 370 °C

-Mutagenic dangerous for environment.

3).Diethyl phthalate

-DEP, phthalic acid diethyl



picture 3: the structure of diethyl phthalate(DEP)

-$C_{12}H_{14}O_4$

-Molecular weight = 222.24 g/mol

-1 L = 1.12 kg

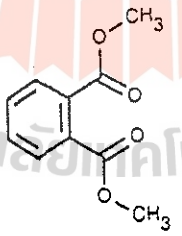
-Melting point -40 °C

-Boiling point 296 °C

-Immiscible with water

4).Dimethyl phthalate

-DMP, phthalic acid dimethyl ester



picture 4: the structure of dimethyl phthalate(DMP)

-$C_{10}H_{10}O_4$

-Molecular weight = 194.19 g/mol

-Melting point 5 °C

-Boiling range/5 hPa 134-138 °C

-Ignition temperature 556 °C

Literature survey

1). Phthalates in infant formulae (Ministry of Agriculture Fisheries and Food, 1996).

Phthalates were detected in all infant formula that were analysed, the most abundant phthalates identified in all sample was di-2-etylhexyl phthalate(DEHP). Using the manufacturers' feeding guide, average intake of total phthalates(expressed as dimethyl phthalate) from infant formulae would be 0.13 mg/kg bodyweight/day for new born infant, falling to 0.10 mg/kg bodyweight/day at six months

The presence of five other phthalates(di-iso-propyl phthalate, dihexyl phthalate, dicyclohexyl phthalate, dihepthyl phthalate and dinonyl phthalate) could be confirm by gas chromatography/ high resolution mass spectrometry, but these compounds were not quantified. Phthalates of higher molecular weight(didecyl, diundecyl and didodecyl isomers) were not detected in any of the samples analyzed.

The toxicity of those phthalate permitted for use in food contact materials has been considered by the EC Scientific Committee for Food(SCF). Sufficient toxicological data were available for the committee to set a Tolerable Daily Intakes(TDI) of 0.05 mg/kg bodyweight /day for DEHP. and a temporary TDI for four of the other phthalate included in his survey: 0.01 mg/kg bodyweight /day for butylbenzyl phthalate; 0.05 mg/kg bodyweight /day for DBP; 0.1 mg/kg bodyweight /day for dicyclohexyl phthalate and 0.2 mg/kg bodyweight /day for diethyl phthalate.

By the date of this article only one of these phthalates, BBP, had been tested in laboratory rodents. Female rats were given BBP at a fixed concentration of 1 mg/l in their drinking water throughout pregnancy and lactation . Resulting intake were estimated to range from 0.1 to 0.4 mg/kg bodyweight/day during the treatment period . This was reported to cause small reduction in testis weight and sperm reduction in the male offspring, who would have been exposed to BBP via the mother during the entirety of their most vulnerable period of testis development. These studies suggest that BBP and DBP may may lead to estrogen activity.

2). Occurrence of phthalic acid esters in food packaging materials (Gaiduskova et al., 1996)

The set of the sample included 42 packs of sweets, wafer, meat and milk products, frozen products, vegetables, potato chips and further foods preferred by Children. DEHP and DBP were demonstrated in all the sample at concentrations ranging from <10 to 1,000 μg per packing; see in the appendix Table 3

The results of the analyses are presented through separated analyses of printed and unprinted part of the packaging where impossible in most cases, it is evident that printing ink is responsible for increased concentration of PAEs.

Other authors have confirmed the migration of PAEs from packing and printing ink into foods and packing are regard as a major source of food contamination by PAEs.

On 18th August 1994. The Chief Hygienist of the Czech Republic announced the following permissible concentration of DEHP and DBP sum valid until 31st December 1996: fruit, flour, leaf vegetable, alcoholic drinks, vine and dessert wines and food in general(milk, red meat, poultry, alcohol-free beverage beer) 1.0 mg/kg ; root vegetable and potatoes 0.7 mg/kg ; other food 4.0 mg/kg.

3). Phthalates in paper and board packaging (Ministry of Agriculture Fisheries and Food, 1995)

MAFF's Food Safety Directorate has carried out a survey of 100 retail samples of printed paper and board packaging to investigate the types and levels of phthalates present in the packaging. Selected foods packaged in the sample of paper and board were also analysed to determines whether phthalates migrated into the food.

Dibutyl phthalate(DBP) and diethyl hexyl phthalate(DEHP) were identified as the most common phthalate present in paper and board packaging with levels ranging from less than 5 mg/kg to over 2500 mg/kg (see Appendix Table 4). Food packed in these materials were found to be contaminated by the phthalates plasticizers (see Appendix Table 5).

Results and discussion

Analysis of Phthalate and Adipate Ester in Love Starches (Thailand) Limited ' s paper bag.

The Australian Food Industry Science Centre were analysed quantitatively for dimethyl phthalate(DMP), diethyl phthalate(DEP), dibutyl phthalate(DBP), benzyl butyl phthalate(BBP), di-2-ethyl hexyl phthalate(DEHP) and diocyl phthalate(DOP) using gas chromatography-mass spectrometry in the paper bag.

Table 1: Analysis of phthalate and Adipate esters (mg/kg)

Description	DMP	DEP	DBP	BBP	DEHA	DEHP	DOP	Total
Sample 1	nd	1	9	nd	nd	2	nd	12
Sample 2	nd	nd	28	2	nd	3	nd	33
Sample 3	nd	1	9	nd	nd	2	nd	12

source: Australian Food Industry Science Center, 1999

nd = for sample 1 and sample 2 not detected at a detection limit of ~ 0.1 mg/kg

nd = for sample 3 not detected at a detection limit of ~ 0.5 mg/kg

Background substraction of a blank was supplied to all extractions

Table 2 : Description of the bag samples

Description	Product	Source	Construction
Sample 1	-	Indonesia	-
Sample 2	Glaci Gel	Thailand(LST)	Multiwall paper bag (4 ply) with 1 polyethylene liner between 2nd and 3rd ply. Outer paper hasprinted surface
Sample 3	Glaci Gel	Thailand(LST)	Multiwall paper bag (4 ply). Outer paper has printed surface

source: Australian Food Industry Science Center, 1999

The results showed that DEP, DBP, BBP and DEHP were found with and BBP in the paper bag with and without plastic liner. The total phthalates in sample 1 and sample 3 (12 mg/kg) are not over the limit but total phthalates in plastic film with paper bag (sample 2 have 33 mg/kg) is over the limit of Love Starches (Thailand) Limited (15 mg/kg) and adipates were not detected in any of the sample tested see in Table 1.

Phthalates and adipates also used as plasticizers in plastic liner, printing ink and adhesive. They can migrate and contaminate into food products. Although the concentration of phthalates and adipates in foods depends on the fat content, moisture content, the contact area etc. but the starches did not contact to the plastic liner, printing ink and adhesive directly, starch is low fat and low moisture so the starch is therefore low risk.

Recommendation

Must be use new plastic liner and test before use to make sure that plastic liner do not contain plasticizers

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Appendices

OCCURRENCE OF PHTHALIC ACID ESTERS IN FOOD PACKAGING MATERIALS

Materials and methods

Packaging material for the analysis of PAEs were collected

- aluminium foil
- plastic wrap
- paper

The packaging were cleaned before the analysis using method dependent on their types and on the content of the packing (rinsing with water and drying, cleaning with cotton-wool soaked with ether, etc.).

Chemical

Analytical standard:

- di-2-etylhexyl phthalate(DEHP)
- dibutyl phthalate(DBP)
- butylbenzyl phthalate(BBP)
- diethyl phthalate(DEP)
- dimethyl phthalate(DMP)
- Chloroform, acetone, dichloromethane were pesticide grade
- n-hexane, methanol were LC grade

Cleaning of glass and chemicals.

1. Heated flasks and test tubes in an oven at 390 °C for 4 hours
2. Rinsed the flask and test tubes with acetone before use.
3. Rinsed the pipettes with acetone.
4. Wash glass wool with chloroform.
5. All organic solvents were distilled in a glass apparatus before use.

Instruments

1. Liquid chromatography
2. Injection loop 10 μl
3. Chromatographic column separon SGX C18, grain size 5 μm
4. Diode array detector polychom 9060
5. Gas chromatography Varian 3400
6. Mass spectrometer
7. Rotation vacuum evaporator

Qualitative detection of PAEs.

A sample(approximately 0.05 g) was dried in an oven at 70 °C for 4 min. The sample was weighed after cooling in a desiccator and put into a 100 ml flask. PAEs were eluted with chloroform at room temperature for 12 hours. The content was shaken occasionally and the flask was put into a mechanical shaker for the last 30 min. The rest of the sample were taken out of the flask with forceps, rinsed with chloroform into the flask and dry in an oven at 70 °C for 70 min. The sample was weighed again after cooling in a desiccator and the extrusion loss was calculated. The loss corresponds to the amount of the plasticizers in the sample:

$$\%(PAEs) = \frac{m_1 - m_2}{m_1} \times 100$$

where m_1= sample weight before elution

m_2= sample weight after elution

The chloroform eluate was dried and the residue was dissolved in 5 ml chloroform 50 μl of the chloroform eluate were transfer into a test tube with ground stopper, chloroform was evaporated with a gentle stream of nitrogen and the residue was dissolved in 2 ml hexane for HPLC determination.

Quantitative determination of PAEs

1. A pack or a sample was cut into pieces and put into a 250 ml. to 500 ml Erlenmayer flask.
2. PAEs were extracted with the 1:1 mixture of hexane and dichloromethane
3. The flask was shaken for 1 hour and the liquid was decanted into a 100 ml flask through a funnel with a bunch of cotton wool.
4. The complete extraction procedure was repeated twice and three extracts were pooled and evaporated in a water bath at 40 °C
5. The residue was dissolved in hexane for HPLC determination purity checks of glassware were done along with each analysis to eliminate the risk of contamination by PAEs.

HPLC conditions

Column: separon SGX C18, grain size 5 μm. length 150 mm, diameter 3 mm.

Detector: UV(diode array)

Wave length:224 mm

Mobile phase:11.3% methanol in hexane

Flow rate: 0.5 ml / min.

The peak area were measured and the concentration of PAEs were derived from calibration curve constructed from at least four points within the concentration range of 0 to 100 mg PAEs per kg. The response of UV detector was linear within this range.

Parameter of the method

Regression coefficients for individual PAE calibration curves within the concentration range of 0 to 100 mg/kg were r = 0.998 to 1.000

The detection limit for quantitative determination of PAEs was 0.1 μg per 1 g of the sample.

The identity of PAEs was confirmed by mass spectrometry(capillary column DB-5, 60 m x 0.25 mm: film 0.25 μm : injector temperature 200 °C, injection on column 2 μl; carrier gas He; working pressure 10^{-5} Torr; source temperature 200 °C; 70 eV; emission 10 μA; interface 250 °C).

Table 3: Concentrations of DEHP and DBP in packaging materials

Product	Type of Package	µg/packing(*µg/g of packing)	
		DEHP	DBP
Sweet and wafers			
-chocolate 1	Plastic foil	291	1,071
-chocolate 2	Plastic foil	348	747
-chocolate 3	Plastic foil	174	881
-Biscuit(vanilla)	Plastic foil	2,712	141
-Biscuit(cocoa)	Plastic foil	2,619	36
-Biscuit(chocolate)	Plastic and Al foil, paper	180	2,349
-Spouge biscuits	Plastic bag	351	1,062
-Biscuit	Plastic bag	2,754	1,212
-Wafer(chocolate)	Plastic foil	1,182	36
-Wafer(nut chocolate)	Plastic foil	2,550	180
-Wafer(cocoa)	Plastic foil	198	1,308
- Wafer	Plastic and Al foil	2,154	57
Meat product			
-Rolled pork	Plastic foil	1,035	615
-Liver salamin 1	Plastic foil	132	69
-Liver salamin 2	Plastic foil	1,629	6
-Salami 1-foil	Plastic foil	62.3*	40.3*
foil with printing	Plastic foil	78.2*	57.2*
-Salami 2-foil	Plastic foil	1,100*	608*
foil with printing	Plastic foil	1,100*	990*
Milk products			
-Milk 1	Cardboard box, plastic foil	1,038	63
-Milk 2	Plastic bag	273	59
-Milk 3	Plastic bag	549	303
-Cheese(steamed, smoked)			
-foil	Plastic foil	52.9*	354.2*
-foil with printing	Plastic foil	215.1*	1.9*
-Cheese(Eidam type 1)	Plastic foil	55.6*	168.9*
-Cheese(Ediam type 2)	Plastic foil	104.9*	16.3*

Table 3: (Continuous)

Product	Type of Package	µg/packing(*µg/g of packing	
		DEHP	DBP
Frozen product			
-Vegetables 1	Plastic bag	70	720
-Vegetable 2	Plastic bag	690	780
-Ice cream 1	Plastic foil	3,027	2,034
-Ice cream 2	Plastic foil	2,025	135
-Ice cream 3	Plastic foil, paper	102	87
-Ice cream 4	Plastic foil, paper	1,308	117
-Ice cream 5	Plastic foil, paper	93	48
-Ice cream 6	Plastic foil, paper	90	42
Sheet paste	Plastic foil	90	36
Other foods			
-Potato ship 1	Plastic bag	2,994	45
-Potato ship 2	Plastic bag	114	1,509
-Potato ship 3	Plastic bag	3,195	93
-Dry pancake mix	Plastic bag	2,313	12
-Rice pudding	Cardboard box	2,829	693
-Potatoes 1	Plastic bag	27.8*	53.8*
-Potatoes 2	Plastic bag	40.2*	99.5*

Source: Guiduskova et al., 1996

Table 4: Concentration of phthalates found in paper and board packaging

Food types	Number of samples	Concentration (mg/kg packaging)	
		Dibutyl phthalates	Diethyl phthalates
Bakery product and snack	20	<5-200	<5-2620
Confectionery	17	20-500	10-2550
Meat and Fish products	7	nd	nd

Source: Ministry of Agriculture Fisheries and Food, 1995

Table 5: Concentration of phthalates found in food packed in paper and board

Food types	Number of samples	Concentration (mg/kg food)	
		Dibutyl phthalate	Diethyl hexylpthalate
Bakery product and snack	5	<0.02-0.9	0.4- 25
Confectionery	7	<0.02-5.8	0.1- 6.7
Meat and Fish product	2	0.05, 4.4	0.8-0.2
Fat	5	outer 1.5-8.4	outer 2.0- 6.1
		core 1.4- 8.7	core1.5-11
Pasta and Cereals	2	<0.02-0.5	0.1, 1.7
Dried fruits	1	<0.02	<0.02
Flour and sugar	2	0.2	0.8, 1.8
Gravy granules and permesan cheese	5	0.8-62	0.2- 22
Micellaneous	2	0.04, 10	1.1-0.9

Source: Ministry of Agriculture Fisheries and Food, 1995

Note:

1. Limit of detection for DBP and DEHP was 0.02 mg/kg food
2. These products have been grouped together as they are packaged in the same type of packaging
3. This group consists of one sample of an ice lolly vegetable burger mix.

Part 2

Introduction

Love Starches (Thailand) Limited produced many types of modified starch from tapioca starches and waxy maize starches. Love Starches (Thailand) Limited is placed at 909 Moo 15, Teparak Road, T. Bangsoathong, King A. Bangsoathong, Samutprakarn, Thailand. The modified starches can be use in confectionery, frozen foods, salad dressings, sauces, meat pies, canned foods and dairy products and other foods, see in picture 5.

picture 5: food products from modified starches.

Mr. Alan Colwell is my co-op supervisor. He is an Australian and works as the director of Love Starches (Thailand) Limited for the company structure see in picture 6.

I worked at Love Starches (Thailand) Limited from 12th January 1999 to 30th May 1999.

Learning Objectives

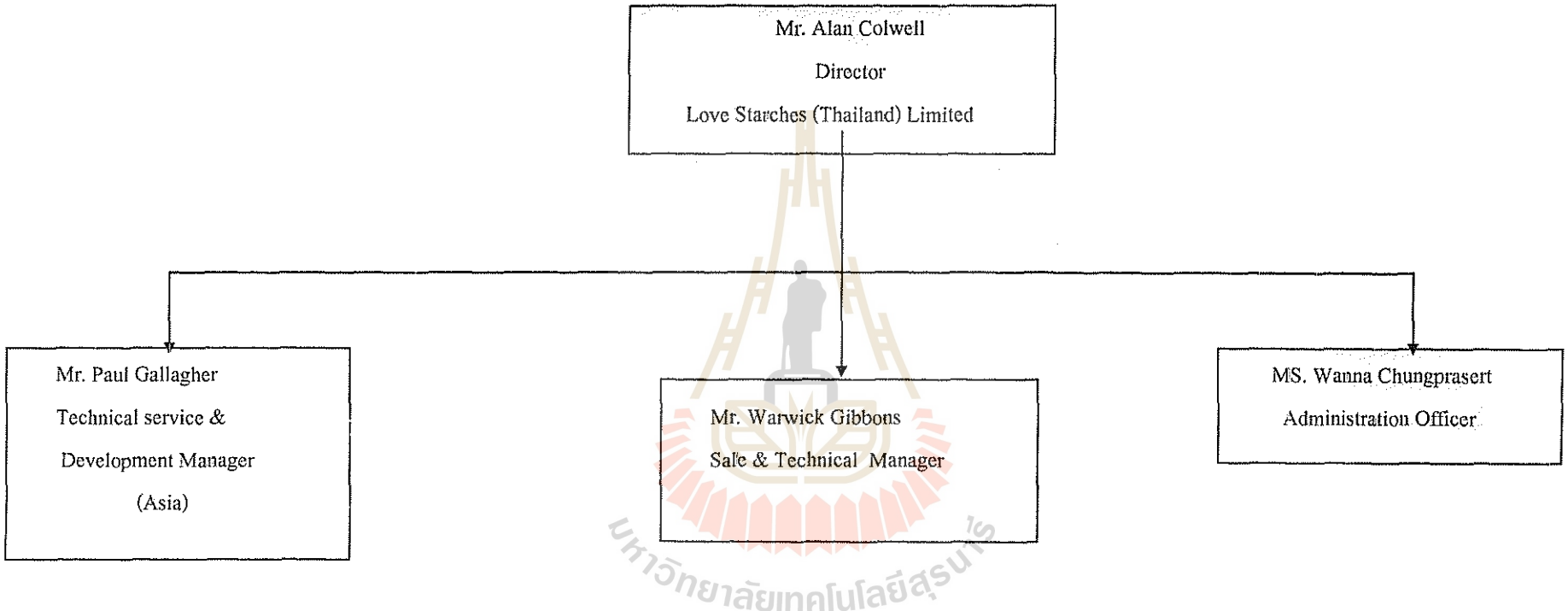
1. Interpersonal skill
2. Communication skill
3. Self-discipline
4. Foreign language

Job description

Quality Assurance assistance, I worked in Love Starches (Thailand) Limited, I was responsible for sampling and testing pH, moisture contents, black specs after drying.

When I worked in the office, I responded for the report about plasticizer (phthalates and adipates) in Love Starches (Thailand) Limited' s paper bag and then find the information about plasticizers (phthalate and adipate esters)from many places for example Kasetsart University, Suranaree University of Technology and Ministry of Public Health. When we know about their dangerous, then go to see the supplier and told him about the problems and then try to get rid off plasticizers from the bags and ask the supplier for letter of guarantee. Phthalates and adipates can also migrate from plastic into the foods. They can cause many carcinogen and weak estrogenic activity. Love Starches (Thailand) Limited concerned about these problems so the they want to get rid off the plasticizers to the acceptance limit (not over 15 mg/kg), it is good for customer's health.

Organization management of Love Starches (Thailand) Limited.



picture 6 : Organization Chart

LOVE STARCHES (THAILAND) LIMITED

909 Moo 15, Teparak Road, T. Bangsaothong, King A.. Bangsaothong, Samutprakarn 10540 Tel. 706-1171-2 Fax. 706-1173

FAX OUT

Fax

To: Mr. Taveesak Mekthon **From:** Roongfa La-khunlek

Fax: 2893911 **Pages:** 1 included this page

Phone: 2893910 **Date:** April 20, 1999

Re: Letter of guarantee (certification) **CC:**

✓ **Urgent** ☐ **For Review** ☐ **Please Comment** ☐ **Please Reply** ☐ **Please Recycle**

Dear Mr. Thaveesak,

Thank you for your attention at our meeting on 7th April 1999 with Mr. Colwell regarding phthalates and adipates in packaging materials

Could you please provide letter of guarantee that Kadard Rungrogn Company Limited will/do not use phthalates and adipates in the manufacture of packaging materials for Love Starches (Thailand) Limited.

Look forward to receiving your letter of guarantee.

Best Regards,

รุ่งฟ้า ลาคุณคลึก

Roongfa La-khumlek