Treatment of phthalic anhydride residue for improved handling and disposal.

by

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Submitted in partial fulfilment of the requirements
for the degree of Master of Engineering (Environmental Engineering)
in the Faculty of Engineering, Built Environment and Information Technology

University of Pretoria

December 2001

Acknowledgements

I want to thank God for giving me the strength and courage to complete this degree successfully.

Thank you to Francois, who has sometimes spent late nights to make sure that what I wrote, made sense.

I also want to write a special word of thanks to the personnel of the company where the research was conducted for all their patience with the trials and their encouragement.

Last I want to thank all the family and friends for their encouragement, love and prayers.

Treatment of phthalic anhydride residue for improved handling and disposal.

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Synopsis

The handling and disposal of hot tarry liquid residues can be problematic in industry, in this case, a phthalic anhydride plant using naphthalene as feed stock. The residue from the plant contains an appreciable amount of phthalic anhydride which desublimates from the residue during draining, resulting in an unsafe working environment. In addition, the residue is a hot liquid that solidifies upon cooling, causing additional risks to personnel during handling and various problems associated with disposal. Research was conducted into finding a treatment method to reduce or eliminate the desublimation of phthalic anhydride from the residue and addressing the hot liquid residue, making the residue safer to handle and easy to dispose of. Laboratory experiments showed that the addition of Dicalite 4151 (a filter aid) in a concentration of 0,3 kg Dicalite 4151 per kg phthalic anhydride residue, resulted in the formation of a powdered residue. This was confirmed during plant trials where using the same concentration proved that a powdered residue could be obtained, while at the same time desublimation of the phthalic anhydride from the residue was negated by distilling the product from the residue mixture. An opportunity exists to test the use of filter aid in other residue producing industries to determine if the same results can be achieved.

KEYWORDS: residue, phthalic anhydride, filter aid, Dicalite 4151, desublimation

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CHAPTER 1
Introduction

Phthalic anhydride is used to a great extent in the manufacture of phthalate plasticisers (Barron *et al.*, 1995). It is derived mainly from o-xylene (obtained from the refining of crude oil), because of its availability on international markets. However, naphthalene, a cheaper raw material substitute, can also be used when available. Consequently, the process using naphthalene feed stock is a more a more cost-effective operation. This is the case at the phthalic anhydride plant where the research for this thesis is conducted.

A further advantage of using naphthalene as feedstock is the highly selective process of the partial oxidation of naphthalene. The partial oxidation of naphthalene leads to the formation of a small number of by-products in contrast with the huge number of by-products formed with the oxidation of o-xylene (McKetta,1991). However, in contrast to phthalic anhydride derived from o-xylene, the partial oxidation of naphthalene and subsequent distillation of the crude product leaves a residue, which is cumbersome to dispose of (van Staden, 2001). The residue also contains an appreciable amount of product (50 to 80 percent in weight). Due to the physical and chemical properties of phthalic anhydride, the product in the residue desublimates on cooling, during the process of draining the residue into disposal trolleys, and results in the release of hazardous fumes and the formation of a light crystalline characteristic mass (McKetta, 1991). This leads to the following problems:

- the phthalic anhydride fumes poses a health risk to the personnel working in the vicinity of the plant where the draining of the residue takes place (Sittig, 1979; CSDS, 1956),
- the fumes can form an explosive mixture with air (Kroschwitz and Howe-Grant, 1996),
- the light crystalline characteristic mass formed, settles onto plant structures and leads to corrosion when in contact with water, and

- the draining procedure and handling of the hot liquid residue is hazardous to the personnel involved in these procedures (van Staden, 2001).

Another example of problems associated with phthalic anhydride residue, is those experienced by other companies in the world, where the residue is collected in the main distillation kettles over a period of time, whereafter it is solidified and dug out for disposal (Owens, 2000). The procedure is very labour intensive.

The objective of this thesis is to address the phthalic anhydride residue problem by developing a treatment method to reduce or eliminate the desublimation of the phthalic anhydride in the residue and obtaining a residue that is safer to handle and dispose of. (The term disposal in this document refers to actual discharge from the plant equipment.)

In this thesis a literature survey is presented in Chapter 2 to provide background to the process and source of the phthalic anhydride residue. The experimental set-ups used during laboratory tests and plant scale testing for treating the residue is discussed in Chapter 3.

The results achieved in performing the laboratory and plant scale experiments are addressed in Chapter 4. Conclusions reached during the laboratory and plant scale experiments as to the successful treatment of the phthalic anhydride residue are presented in Chapter 5.

CHAPTER 2
Literature survey

2.1 THE HISTORY OF PHTHALIC ANHYDRIDE

In the nineteenth century, phthalic anhydride, presently used mainly for the production of phthalate plasticisers and resins, were essentially derived from naphthalene. The process involved the oxidation of naphthalene with chromic or nitric acid. However, this process was very expensive. Researchers thus began to investigate means to manufacture phthalic anhydride more economically to stimulate the growing demand of phthalic anhydride as an intermediate for dyes. In 1896, BASF in Germany patented a method in which naphthalene was oxidised with 100% sulphuric acid at 250°C to 300°C (Donaldson, 1958). The reaction took place in the presence of mercuric sulphate, which produced by-products such as carbon dioxide and sulphur dioxide. With the cheaper process, the development and production of synthetic indigo dyes started to increase rapidly. Unfortunately for the American and British consumers, the First World War meant that phthalic anhydride supplies from Germany were cut off.

In order to secure their own supply of phthalic anhydride, researchers in America succeeded in developing a vapour-phase catalytic process for the large-scale production of phthalic anhydride in 1917. At the same time, Wohl from I.G. Germany had developed a similar process to the one in America. In the competition to develop the phthalic anhydride process, Wohl could prove that he was the first to make the process work. His patent was granted priority over and above the American companies (Donaldson, 1958).

Conover and Gibbs published their development of the American process in 1922. This process involved the oxidation of naphthalene vapour and a four-fold excess of air passed over a molybdenum oxide or vanadium pentoxide catalyst at 350°C to 500°C (Donaldson, 1958). This process still forms the basis for phthalic anhydride production.

Then in 1946, the air oxidation of 90% pure o-xylene to produce phthalic anhydride was commercialised. An advantage of using o-xylene was that it gave a theoretical yield for phthalic anhydride of 1,395 kg/kg, in comparison with the yield from using naphthalene of 1,157 kg/kg (Kroschwitz and Howe-Grant, 1996).

Until the late 1950's, naphthalene derived from coal tar was the preferred feedstock for the manufacture of phthalic anhydride in both Germany and the United States. However, in the 1960's a shortage of naphthalene feedstock started to occur. Companies were forced to use o-xylene as feed, which were produced by a growing petrochemical industry. Since then, large quantities of o-xylene has been made available at competitive prices, making it the predominant feed material for the production of phthalic anhydride with naphthalene contributing only in limited amounts. For instance, in 1995, 83% of the phthalic anhydride produced in the United States were derived from o-xylene as feed material. In Western Europe, 93% of the phthalic anhydride produced was derived from o-xylene (Barron *et al.*, 1995).

At present, some companies operate a feedstock mixture, whereby their process can use either a mixture of o-xylene and naphthalene or any of the feedstock separately. The use of a mixture of o-xylene and naphthalene contributes to a certain amount of flexibility, especially when one feedstock is either expensive or not readily available.

2.2 USES OF PHTHALIC ANHYDRIDE

During the early years of production, phthalic anhydride was mostly used in the manufacturing of dyes. However, new end-products evolved until, for example, 54% of the total production of phthalic anhydride by the U.S.A. in 1994 was used to produce phthalate plasticisers (Barron *et al.*, 1995). Phthalate plasticisers are used predominantly for the production of flexible PVC compounds, and to a lesser extent for cellulose acetate, polyvinyl acetate, and cellulose nitrate compounds (CS, 1995).

The most widely used phthalate ester is a branched dioctyl phthalate, di(2-ethylhexyl) phthalate. It is considered as the standard PVC (polyvinylchloride) plasticiser. Generally, di(2-ethylhexyl) phthalate is used to produce products like sheeting, film and coated fabrics because it permits higher production rates of the end products (Barron *et al.*, 1995). Other important phthalate plasticisers are ethylene-based linear alcohol esters in the C_6 – C_{11} range such as diisononyl phthalate and diisodecyl phthalate. The linear phthalates are widely used for automotive vinyls and dispersion coatings as well as other calendered and extruded products requiring low-temperature flexibility. Diisononyl phthalate and diisodecyl phthalate have become major general-purpose plasticisers, because of their processing and performance characteristics.

According to Barron *et al.* (1995), unsaturated polyester resins are also manufactured using phthalic anhydride. These unsaturated polyester resins are reinforced with glass for applications in the marine industry, construction, transportation, consumer goods and electrical components.

Another product using phthalic anhydride as raw material, is non-reinforced plastic. Major markets for these include synthetic marble, cast furniture components, bowling balls and automobile repair putty.

Some alkyd resins are produced by reacting phthalic anhydride with polyhydric alcohols and fatty oils or acids. An estimated 80 – 85% of alkyd resins are produced by using phthalic anhydride. Ninety five percent of all alkyd resins produced are consumed for the production of surface coatings. The largest market for alkyd surface coatings is in traffic paints.

Other smaller consumers of phthalic anhydride include:

- polyester polyols which are used as a raw material for polyurethane resins,
- dye intermediates and pigments,
- halogenated anhydrides which are used to produce flame-retardant rigid polyurethane foams,

- isatoic anhydride which is produced by reacting phthalic anhydride with ammonia and is used to manufacture saccharin and insecticide,
- polyetherimide resins supplying electrical/electronic, medical and aviation applications, and
- small-volume applications such as di-allyl phthalate, phenolphthalein, phthalimide, cellulose acetate phthalate and 4-sulfophthalic acid.

2.3 ECONOMICAL FACTORS AND PHTHALIC ANHYDRIDE DEMAND

Supply, demand and availability of feed material affects the world market value of phthalic anhydride greatly. A large supply of product might mean that the price of phthalic anhydride at that stage has a lower price, whereas a small supply of product will necessarily increase the price. This small supply in product can be caused by either a shortage in feed material, supply and demand or certain external factors.

The price of phthalic anhydride is greatly dependent on the price of crude oil, since the predominant feed material for phthalic anhydride, o-xylene, is derived from crude oil. Therefore, when the OPEC (Oil Producing and Exporting Countries) members decide that crude oil production should be increased, the crude oil prices, and consequently the o-xylene price, will drop. This was the case during June/July 2000 when the OPEC members announced an increase in crude oil output. As a result of this, o-xylene production increased and the price of o-xylene dropped from between $460 – $470/ton free on board to the lower $400's/ton free on board in Western Europe (Ockerbloom, 2000; Tecnon, 2000).

The price of phthalic anhydride in South Africa is determined by the Northwest European phthalic anhydride prices. Another factor influencing the selling price is South Africa's fluctuating exchange rate. Although the world price for phthalic anhydride might be low, a high exchange rate for South Africa's currency could result in the selling price of phthalic anhydride remaining high.

In the next five to ten years, issues that might affect the world market of phthalic anhydride include (CEH, 2000), *inter alia*:

- the fluctuating price of the main raw material, o-xylene,
- limited quantities of naphthalene captively produced,
- improving catalyst technology,
- growing markets for phthalic anhydride derivatives in South America and Asia,
- competition from dicyclopentadiene as a phthalic anhydride alternative in unsaturated polyester resin formulations,
- increased use of powder coatings and other environmentally friendly technologies that do not consume phthalic anhydride derived resins,
- possible environmental regulations affecting the manufacture of polyvinylchloride (PVC), especially in Europe, and
- substitution of metallocene-based polyolefins in certain flexible PVC markets.

Although there are no environmental issues affecting the production of phthalic anhydride directly, stronger environmental regulations on end-uses for phthalic anhydride might inhibit the growth rate somewhat. This is especially true with di-octyl phthalate, a primary plasticiser. Stringent environmental regulations have been applied regarding the handling, use and disposal of the material (EPA, 1994a).

Great concerns arose with the use of other phthalates like di-isononyl phthalate (DINP), to soften some plastic toys and other children's products (CPSC, 1998). However, studies have shown that the low amounts of chemical that can be ingested are not harmful. Therefore, the United States Consumer Product Safety Commission (CPSC) did not recommend a ban on these products, but as a precaution, requested the industry to remove phthalates from soft rattles and teethers.

The development and manufacture of non-phthalate plasticisers as substitutes will also affect the demand for phthalic anhydride (EPA, 1994a). Alternatives

to phthalates will also have to conform to performance requirements and demonstrate themselves to be safe. Another requirement is that the plasticiser must be compatible with PVC and relatively efficient at softening it. Up until May 1999, suitable alternative plasticisers were not readily available (ECPI, 1999).

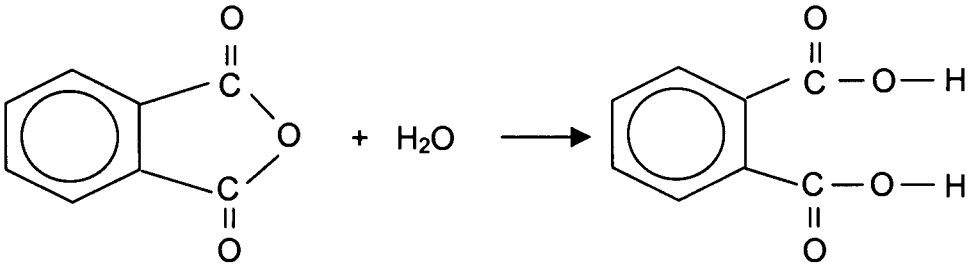
Apart from the above factors, the production of phthalic anhydride continues to increase, as can be seen from the world production for 1993 and the estimated production for 2000 of phthalic anhydride, given in Table 2.1 (CS, 1995). In 1995, for example, a growth in phthalic anhydride production of up to 4,3% was anticipated in China.

Table 2.1 World production of phthalic anhydride.

COUNTRY	**1993 (thousand metric tons)**	**2000 (thousand metric tons)**	**Average Annual Growth Rate, % (1992 - 2000)**
U.S.A.	387	498	2,6
Western Europe	745	820	1,2
Japan	277	341	1,2
China	197	243 (1997)	4,3 (1992 - 1997)
Latin America	341 (1994)	-	-

2.4 PHYSICAL PROPERTIES OF PHTHALIC ANHYDRIDE

Phthalic anhydride is an organic compound with chemical formula $C_8H_4O_3$. It is a white crystalline solid with a low vapour pressure (12 kPaa at 200°C) and a relatively high melting point of 130,8°C, which tends to sublimate on heating. The boiling point at 101,3 kPa is 284,5°C and the density at 150°C, where it is in the liquid state, is 1 118 kg/m^3 (Perry, 1984). When phthalic anhydride vapour is cooled in contact with air, it desublimates and creates a characteristic "snow" which may cause corrosion of plant structures when washed off with water. Corrosion occurs because of phthalic acid formation when phthalic anhydride is exposed to water, according to Equation 2.1.



2.1

Phthalic anhydride + Water ⟶ Phthalic acid

Phthalic anhydride also poses explosion hazards as either a dust or vapour in air or as a reactant. Table 2.2 presents the explosion hazards of phthalic anhydride dust or vapour (Kroschwitz and Howe-Grant, 1996).

Table 2.2 Explosion hazards of phthalic anhydride dust and vapour.

Property	**Value**
Dust	
Explosibility index	>10
Minimum explosive concentration (g/l)	0,015
Vapour	
Explosive limits in air at 140 – 285°C (vol. %)	
lower limit	1,7
upper limit	10,5

According to Elvers *et al.* (1992), the explosion hazard data of phthalic anhydride in air vary significantly. Explosions can occur at concentrations below 100 g/m^3 air, depending on the impurities present.

2.5 EFFECTS OF PHTHALIC ANHYDRIDE ON HUMANS

The effects of phthalic anhydride on human health and the environment are affected by the following:

- length of exposure,
- frequency of exposure, and

- health of the person or the condition of the environment when exposure occurs.

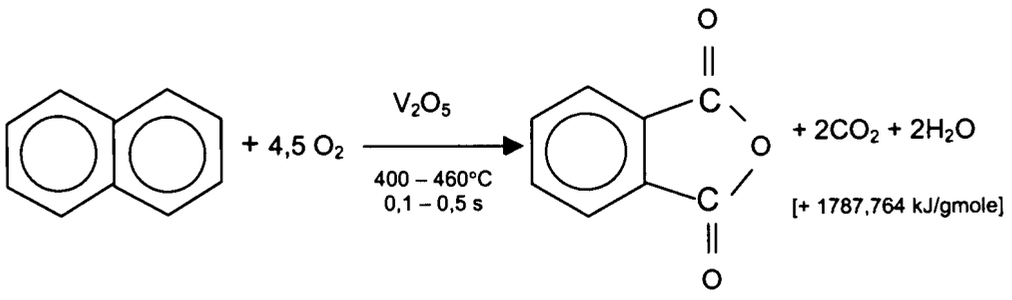
When a person is exposed to phthalic anhydride vapour, for example by inhalation, it results in an acidic reaction with moisture in the mucous membranes forming phthalic acid, according to Equation 2.1.

Subchronic and chronic effects experienced by workers exposed to moderate to high concentrations of atmospheric phthalic anhydride are irritation of the eyes, skin and respiratory tract and development of hypersensitivity, bronchial asthma and emphysema (EPA, 1994b). Studies were done by the American Conference of Governmental Industrial Hygienists on 118 workers, either currently or formerly employed in plants producing alkyd and/or polyunsaturated resins to determine if any respiratory ailments exist (EPA, 1994b). During the study, time-weighted-average breathing zone samples were taken in the above plants in areas where bags containing flaked phthalic anhydride were cut open and emptied manually into reactors several times a day for a 10 to 30 minute period. The samples measured between 3 to 13 mg phthalic anhydride/m^3 of air. Twenty four percent of the individuals experienced rhinitis, 11% had productive bronchitis and 18% had work-associated asthma.

Other symptoms that workers developed after exposure to mixtures of phthalic anhydride and phthalic acid were bloody nasal discharge, hoarseness, coughing, bronchitis and emphysema (EPA, 1994b).

2.6 PROCESS DESCRIPTION

Phthalic anhydride is produced by the partial oxidation of naphthalene or o-xylene with air in the gas phase. The naphthalene-air mixture is passed through a tubular reactor where the exothermic oxidation reaction takes place on a highly selective catalyst. A typical naphthalene oxidation catalyst for fixed bed oxidation is a mixture of vanadium oxide and an alkali metal sulphate on a silica support. The overall reaction is as follows (Austin, 1984):



2.2

There are two major steps in the production of phthalic anhydride:

- the first step is the partial oxidation of naphthalene to produce crude phthalic anhydride (see Figure 2.1), and
- the second step is the distillation of the crude phthalic anhydride to a purified product of at least 99,8% purity (see Figure 2.3).

The oxidation process (see Figure 2.1) begins with the filtering of air used in the process. This is necessary to remove dust and debris that might damage the reactor catalyst. It is then compressed to a pressure of less than 1 atm gauge pressure. After the air is preheated to a temperature of 140°C, the total air stream is split into a primary and secondary air stream. The primary air stream is then fed directly to the gas mixer. To overcome the additional pressure drop across the naphthalene evaporator, the secondary air stream is fed to a secondary air blower. In the naphthalene evaporator, preheated naphthalene is vaporised into the secondary air stream. To achieve the required concentration of naphthalene to air in the total process air stream, the secondary air stream flow is controlled. After vaporisation, the preheated mixture of naphthalene and air is mixed with the main air stream before it enters a fixed bed multi-tubular reactor. This reactor resembles a vertical shell-and-tube heat exchanger with catalyst filled tubes and molten salt in the shell to remove excess heat formed from the highly exothermic reaction.

As the feed mixture (air and naphthalene) enters the reactor tubes, it is heated to the required reaction temperature via heat transfer from the salt. The exothermic reaction inside the reactor starts at between 50°C to 100°C below

the molten salt temperature of approximately 360°C. When the reaction temperature approaches that of the molten salt, the heat transfer from the molten salt to the reaction mixture declines. As the heat generation from the reaction accelerates, resulting in a rapid temperature increase in the reactor, the salt solution becomes the cooling agent for removing heat from the reactor.

After the reaction of the feed mixture has completed in the reactor, the now product gas is further cooled to a temperature of about 175°C in a gas cooler (shell-and-tube heat exchanger).

The phthalic anhydride product is then recovered by desublimation (dew point of the product gas mixture is below the melting point of phthalic anhydride) in the switch condensers. Switch condensers are shell-and-horizontal-tube type heat exchangers with extended surfaces on the outside of the tubes, where the phthalic anhydride is condensed. Heat transfer oil is circulated through the tubes to melt or condense the phthalic anhydride product gas. To maintain a continuous operation, a number of condensers are connected in parallel and alternately switched from condensing service to melting out and re-cooling services. Optimal times for the different operating stages of the switch condensers have been determined by the licensors of the process. When sufficient crude phthalic anhydride has been collected on the fins of a switch condenser in the designed time, it is isolated from the process stream. To melt the phthalic anhydride, the temperature of the heat transfer oil is raised.

The molten product is then drained from the relevant switch condenser. The heat transfer oil temperature is lowered to cool down the condenser before it is returned to service for the next loading stage.

More than 99% of the phthalic anhydride in the reaction stream is removed with the switch condensers. The recovered crude phthalic anhydride is stored in steam-heated tanks or fed directly to the distillation plant.

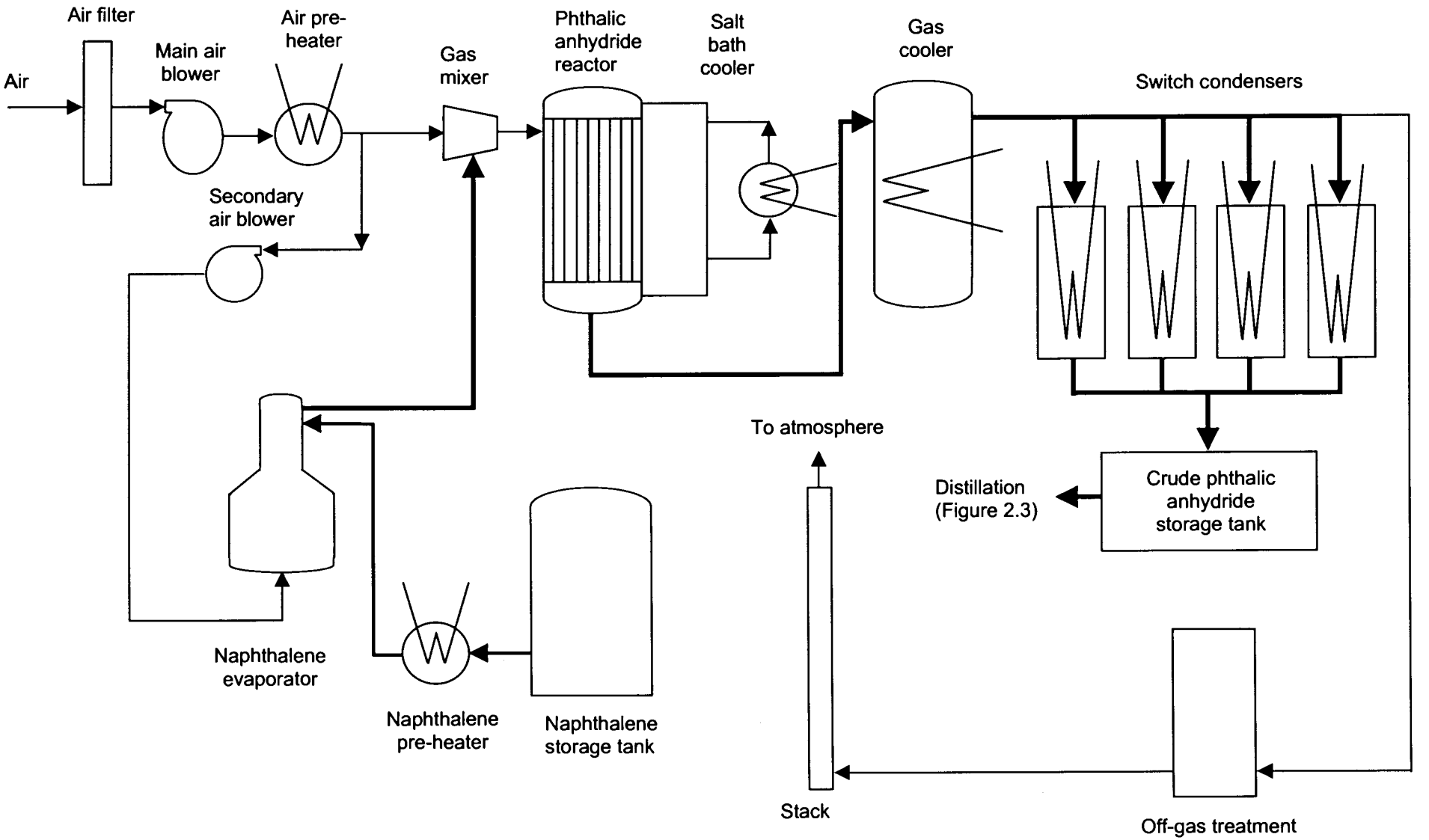


Figure 2.1 Flow diagram for the partial oxidation of naphthalene.

Due to thermodynamic and mechanical slippage, a small fraction of the phthalic anhydride in the reaction gas is not collected in the switch condensers. Light organic by-products formed in the reactor, which are primarily benzoic acid, maleic anhydride and naphthaquinone, are also not collected in the switch condensers due to their chemical properties. Benzoic acid and maleic anhydride are formed from the over-oxidation of phthalic anhydride. Naphthaquinone is formed as a result of the partial oxidation of naphthalene, according to the reactions shown in Figure 2.2. These by-products are also known as the light boiling impurities of phthalic anhydride. The higher boiling impurities include a number of carboxylic acids along with tarry carbonaceous residue, which forms part of the final residue after distillation of the product. The light boiling impurities have to be treated to acceptable environmental levels before it can be vented to the atmosphere via a stack. Treatment takes place via either water scrubbing, thermal incineration or catalytic incineration, depending on the preference of the plant owners.

Apart from the above by-products, phthalic acid is also a major impurity of crude phthalic anhydride. Phthalic acid is formed by the reaction of phthalic anhydride with the water vapour present in the reaction gas, according to Equation 2.1. This happens when there is a cold spot present in the equipment, due to a lack of sufficient heating. The water condenses at the cold spot and reacts with the phthalic anhydride to form phthalic acid. This reaction is unfavourable because the acid formed attacks the iron of the construction materials of the equipment to form pyrophoric compounds. Pyrophoric compounds can self-ignite, therefore creating explosive, flammable conditions.

The next step after collecting the crude phthalic anhydride from the switch condensers is the distillation of the crude phthalic anhydride to commercial grade. Distillation consists of three consecutive steps:

- thermal treatment to convert the remaining phthalic acid to phthalic anhydride,

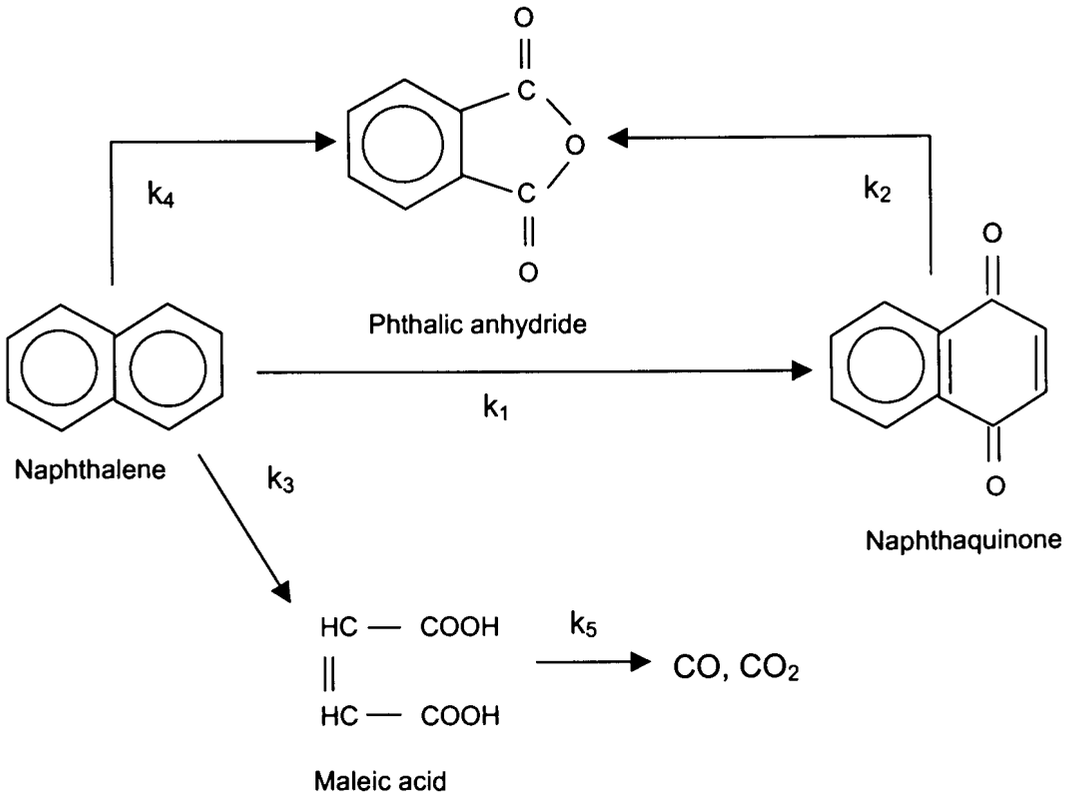


Figure 2.2 Partial oxidation reactions of naphthalene (McKetta, 1991).

- light ends removal by distillation under vacuum, and
- removal of pure product by distillation under vacuum.

The crude phthalic anhydride is first pre-treated in a pre-treatment kettle where the by-product, phthalic acid, is converted to phthalic anhydride (see Figure 2.3). Decomposition of phthalic acid takes place at a temperature above 220°C. Addition of chemicals can then take place, if required, to polymerise naphthaquinone to a high boiling residue. Different chemicals can be used, depending on the process licensor, to help in the formation of a high-boiling residue. Some of these chemicals include, *inter alia*, sodium hydroxide, sodium carbonate and sulphuric acid (Elvers *et al.*, 1992).

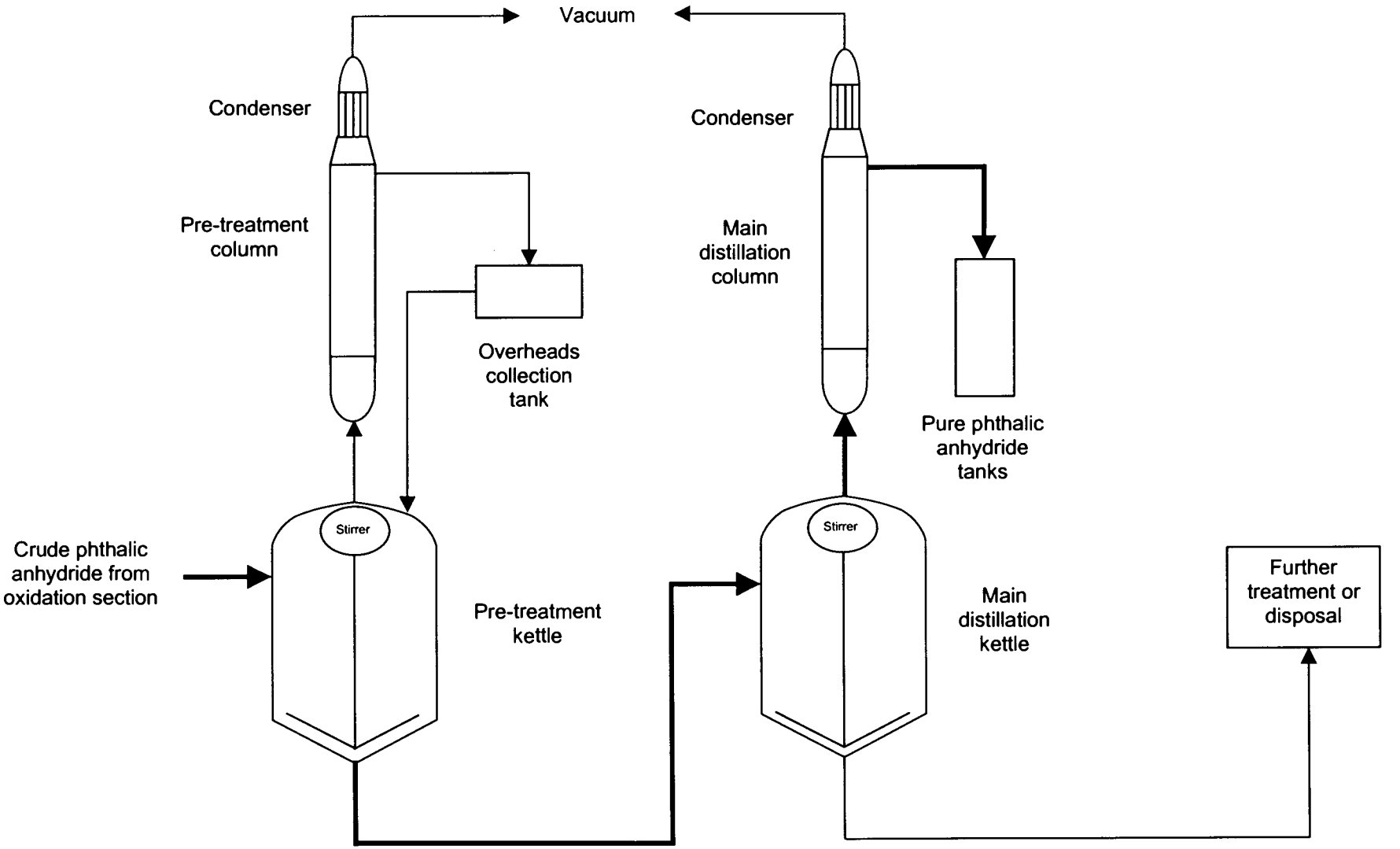


Figure 2.3 Flow diagram for the distillation of crude phthalic anhydride.

After pre-treatment with chemicals has been completed, the low-boiling constituents such as maleic anhydride and benzoic acid are distilled off through the pre-treatment distillation column. The bottoms of the pre-treatment kettle are then introduced into the main distillation kettle from which pure phthalic anhydride are removed at the head of the main distillation column with further distillation.

The pure phthalic anhydride product is stored either as a liquid in pure phthalic anhydride tanks for distribution to customers, or flaked and bagged in 25 kg or 500 kg bags.

Various methods have been developed and tested to treat the residue that remains after distilling off the pure phthalic anhydride product. These methods include, *inter alia*:

- further distillation of the residue to retrieve any product left in the residue to produce a phthalic anhydride-free residue ready for disposal (Truman, 1970),
- incineration (McKetta, 1991),
- spray evaporation (Ackermann, 1965), and
- utilisation of the residue as raw material for other products such as powder dyes (Pavlovich *et al.*, 1996).

2.7 PROBLEMS ASSOCIATED WITH PRESENT PLANT

Problems associated with the final treatment of the remaining residue depends on whether phthalic anhydride was derived from either o-xylene or naphthalene. The higher quality and different by-products formed from the use of o-xylene as raw material produces residue with less of a problem as that formed from naphthalene, since the quantity of residue formed is much less. The emphasis of this thesis will be to investigate possible solutions to the problems experienced with the treatment of the final residue derived from using naphthalene as raw material.

The phthalic anhydride plant at which the residue problem is investigated was originally designed with a residue distillation section for treatment of the final residue. However, as technology changes to the catalyst used in the reactor in the oxidation section took place, problems were experienced in distilling phthalic anhydride from the final residue. Due to mechanical problems experienced with the residue distillation equipment, the treatment of residue was discontinued in 1991 and the residue drained directly from the main distillation kettle into disposal trolleys. On draining, the unrecovered phthalic anhydride (which can range from 50 – 80 mass percent in the residue) desublimates on contact with the much cooler ambient air (see Figure 2.4). This gives rise to the following problems:

- phthalic anhydride fumes which poses a health risk to the personnel working in the vicinity of the draining procedure. Phthalic anhydride fumes are severely irritating to the eyes, respiratory tract, skin, and especially to moist tissues (Sittig, 1979; CSDS, 1956),

Figure 2.4 Draining of phthalic anhydride residue from a main distillation kettle.

- an explosive mixture can be formed with air (Kroschwitz and Howe-Grant, 1996),
- the light crystalline mass that is formed settles onto plant structures and can lead to corrosion, and
- the draining procedure and handling of the hot liquid residue poses hazards to personnel involved in these procedures.

Another example of problems associated with phthalic anhydride residue, is those experienced by other companies in the world, where the residue is collected in the main distillation kettles over a period of time, solidified and dug out for disposal (Owens, 2000). The procedure is very labour intensive.

The problems experienced in the distillation of the phthalic anhydride residue, as well as the experimental set-up used to address these problems, will be addressed in Chapter 3.

CHAPTER 3
Experimental set-up

3.1 EXISTING PLANT

3.1.1 Historical background to experimental set-up

The first modern phthalic anhydride plant, on the industrial site where the experimental set-up is located, was built in 1967 using a pellet type catalyst. With this catalyst, formation of naphthaquinone by-products was almost negligible and thus the pre-treatment of the crude phthalic anhydride product only included heat treatment to decompose phthalic acid that has formed earlier in the process. Occasionally NaOH was added if a problem occurred with naphthaquinone formation, polymerising the naphthaquinone to a non-volatile residue. Distillation of the phthalic anhydride product out of the distillation residue could therefore be accomplished very easily with a separate residue distillation vessel.

Due to growing demands for phthalic anhydride, additional plants were build in 1971 (using a pellet type catalyst) and 1983 (using a spherical type catalyst).

During 1985, the reactor tubes of the 1967 plant ruptured and production was discontinued on this plant. At this time, the catalyst in the 1971 plant was also changed to the spherical type catalyst used in the new 1983 plant, due to technological improvements on these catalysts. (The advantages and disadvantages of the spherical and pellet type catalysts utilised in the 1967 and 1971/1983 plants are shown in Appendix A.) However, problems were experienced with the residue distillation process of the 1971/1983 plants. In contrast with the pellet type catalyst of the 1967 plant, naphthaquinone formation was very high. Therefore, a pre-treatment chemical had to be added constantly to polymerise naphthaquinone to a non-volatile residue. Chemical pre-treatment with Na_2CO_3 produced a distillation residue with zero recoverable phthalic anhydride. This was in contrast with the 1967 plant that produced residue, containing 60 – 80% (m/m) phthalic anhydride, which was 85 – 90% recoverable and easy to dispose of (Lloyd, 1985).

During the 1980's, technology of phthalic anhydride reactor catalysts improved drastically and a new type of catalyst (ring type) were used to replace the spherical type. The advantages of the ring type catalyst were (Tack, 1988; Van der Merwe, 1989 and Wunsch, 1987):

- reduced activity of the catalyst on start-up of the plant, in comparison with the spherical type of catalyst. Theoretically, this meant that the plant could be brought on to production much quicker (six days instead of 23),
- reduced pressure drop over the catalyst bed,
- lower electricity consumption, and
- longer catalyst life.

Shortly after the introduction of the ring type catalysts, production at the 1971 plant was discontinued due to uneconomical operation thereof. Further tests on the distillation of the residue with the ring type catalyst have not been performed since 1991, due to mechanical failures on the residue distillation system (Van der Merwe, 1996).

3.1.2 Plant apparatus

The residue distillation equipment on the plant was chosen as experimental apparatus for the following reasons:

- preliminary trials showed that phthalic anhydride is recoverable out of the residue presently produced with further distillation in the residue distillation kettle (Van Staden, 2001),
- since the problem is experienced at plant scale, laboratory scale equipment will only give a vague idea whether treatment of the phthalic anhydride residue will be successful, therefore leading to ambiguous results,
- a representative phthalic anhydride residue sample has to be taken from the main distillation kettle on the plant and should exposure to air occur, some of the phthalic anhydride in the sample will desublimate, decreasing the actual content of product in the residue. This might lead to ambiguous results obtained in the laboratory, and

- the residue distillation equipment still exist leading to low capital expenditure for suitable equipment.

The experimental set-up used for this thesis is shown in Figure 3.1, with an explanation of the acronyms used in Table 3.1.

Table 3.1 Description of acronyms used in Figure 3.1.

Acronyms	Description
FIC71501	Flow indicating controller for heat transfer oil.
FT	Flow transmitter for heat transfer oil.
HIC71801	Hand indicating controller for compressed air.
II71601	Current indicator for residue distillation kettle agitator – motor amperage.
PI71504	Pressure indicator of residue distillation kettle.
TI71503	Temperature indicator of residue distillation kettle.
TI71701	Temperature indicator of residue distillation dephlegmator.
TI71901	Temperature indicator of residue distillation collecting tank.
SPx	Sampling points.

3.1.2.1 Residue distillation kettle

The residue distillation kettle is a jacketed vessel with limpet coils on the outside. The kettle is heated with hot oil passing through the limpet coils and the flow controlled via FIC71501. To improve the heat transfer rate to the contents of the residue distillation kettle, the contents is agitated with a specially designed agitator, monitored with II71601.

The residue distillation kettle is used primarily to recover any remaining phthalic anhydride out of the residue, transferred from the main distillation kettle. Once the phthalic anhydride has been recovered, the remaining residue is drained into a disposal trolley.

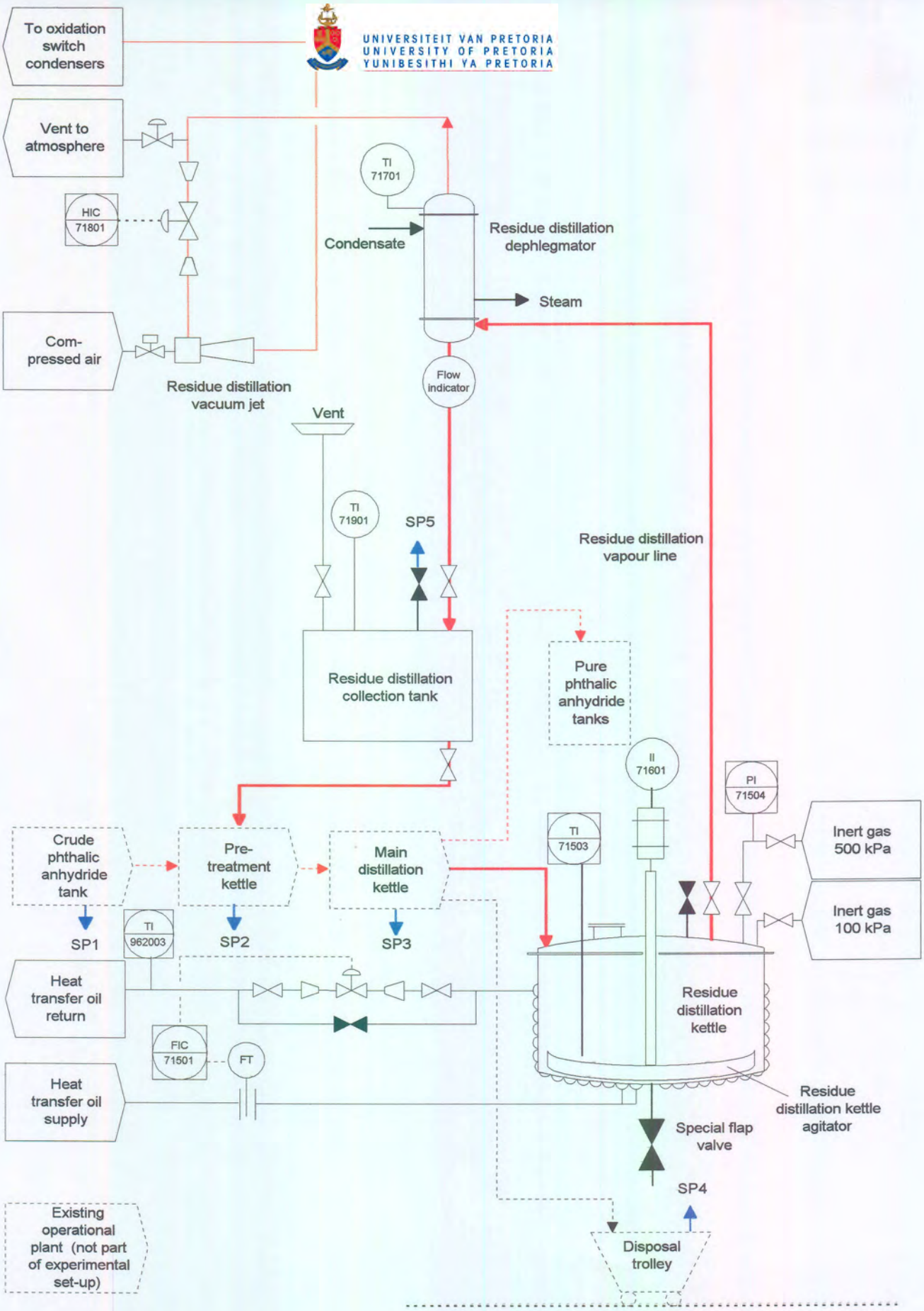


Figure 3.1 Flow diagram of experimental set-up indicating parameters to be measured.

The capacity of the residue distillation kettle is 3,402 m^3. The designed operating conditions for the residue distillation system are as follows:

- residue distillation vapour line temperature 200 – 250°C,
- residue distillation vapour line pressure 0 – 75 kPaa,
- residue distillation dephlegmator temperature 131°C, and
- residue distillation dephlegmator pressure 289,58 kPaa.

3.1.2.2 Residue distillation vapour line

The residue distillation vapour line is a 204,3 mm diameter vapour line. It is used primarily to feed the residue distillation kettle vapours to the residue distillation dephlegmator for condensation of the distilled phthalic anhydride.

3.1.2.3 Residue distillation dephlegmator

Phthalic anhydride vapours from the residue distillation vapour line enters the residue distillation dephlegmator (a shell and tube heat exchanger). Condensate is fed to the shell side of the dephlegmator where steam is generated from the latent heat of the molten phthalic anhydride in the tube side.

3.1.2.4 Residue distillation vacuum jet

The residue distillation vacuum jet serves to create a vacuum to lower the boiling point of the phthalic anhydride in the residue distillation kettle. Compressed air at 150°C is supplied to the vacuum jet to prevent cooling of the phthalic anhydride gas and consequent blockages. An air actuated control valve, HIC71801, controls the vacuum.

Non-condensable gases are removed by the vacuum jet from the residue distillation dephlegmator and discharged to the switch condensers in the oxidation section where any phthalic anhydride in the vapours are recovered (see Section 2.6).

3.1.2.5 Inert gas system

The nitrogen inert gas system comprises of two pressures, 100 kPa and 500 kPa. The 100 kPa system is used to break the vacuum created in the residue

distillation system when required. The 500 kPa supply is used for purging instrumentation impulse lines on the residue distillation kettle and vapour line.

3.1.2.6 Residue distillation collection tank

The residue distillation collection tank has a capacity of 2,177 m^3. It is used primarily as a storage facility for the condensed phthalic anhydride from the residue distillation dephlegmator. The recovered phthalic anhydride in the collection tank is fed to the pre-treatment kettles for purification.

3.1.3 Planning

No documentation is available on any experimental work performed on the distillation of phthalic anhydride residue using the existing set-up. Thus, in order to investigate the effect of the process parameters on the ability to retrieve phthalic anhydride, the following fixed process variables were chosen:

- amount of vacuum applied on the residue distillation kettle, controlled with HIC71801 (see Figure 3.1),
- amount of heat transferred to the residue in the residue distillation kettle, controlled with FIC71501 (see Figure 3.1), and
- distillation time.

The following upstream parameters will be monitored for variances that might have an effect on the distillation of the phthalic anhydride out of the residue:

- stability of the oxidation process (any unusual conditions will be noted), and
- naphthaquinone content of crude phthalic anhydride, as this will affect the amount of sodium carbonate added for pre-treatment.

As preliminary trials showed that recovery of phthalic anhydride is achievable with distillation (Van Staden, 2001), the first experiments will be to establish a reference graph of percentage recovered phthalic anhydride against distillation time at the following process parameters:

- running the system under 100% vacuum,
- running the system with a maximum oil flow (9 000 kg/h at 316°C), and

- commencing distillation immediately after a batch from the main distillation kettle has been transferred to the residue distillation kettle. (It was found from experience in the past that it was difficult to recover the phthalic anhydride from the residue if distillation was not started directly after transfer from the main distillation kettle; Lloyd, 1985.)

Further experiments will then be carried out to determine the effect of vacuum on the recovery of phthalic anhydride from the residue. The vacuum will be varied in 20% intervals, from 100% vacuum to 0% vacuum via HIC71801. The graphs drawn of percentage phthalic anhydride recovered against distillation time at the corresponding vacuum pressures will give an indication of the vacuum at which distillation is no longer achievable. The following process variables will also be monitored to determine relationships for optimal operation of the residue distillation system:

- residue distillation kettle pressure with PI71504,
- oil flowrate with FIC71501,
- oil outlet temperature with TI962003,
- residue distillation kettle temperature with TI71503, and
- level of the residue distillation collection tank via manual level measurement.

The level in the main distillation kettle will be measured manually before transfer to the residue distillation kettle to determine the amount of residue that will be transferred to the residue distillation kettle. From a sample (SP3) of the residue in the main distillation kettle, the phthalic anhydride content can be determined. The level of the residue distillation collection tank will be monitored with distillation time. A sample (SP4) of the final residue after distillation will determine the percentage recovery of the phthalic anhydride. The percentage of recovered phthalic anhydride can then be determined by a mass balance using the following equation:

$$\% \text{ Recovered phthalic anhydride} = \frac{\%PA_{SP5} \times M_{PA\ collected}}{\%PA_{SP3} \times M_{PA\ residue\ transferred}} \times 100 \quad 3.1$$

where:

$\%PA_{SP3}$ = percentage phthalic anhydride in residue before recovery (SP3),

$\%PA_{SP5}$ = percentage phthalic anhydride of recovered phthalic anhydride in residue distillation collection tank (SP5),

$M_{PA\ collected}$ = mass phthalic anhydride collected in residue distillation collection tank, and

$M_{PA\ residue\ transferred}$ = mass phthalic anhydride residue transferred to residue distillation kettle.

The following samples will also be collected to determine if the process is stable:

- sample of crude phthalic anhydride before pre-treatment, to check that the oxidation process is at steady state and produces product with consistent contents (SP1),
- sample of pre-treated crude phthalic anhydride in pre-treatment kettle, consisting of phthalic anhydride from residue distillation collection tank and phthalic anhydride from crude storage tank (SP2), and
- sample of recovered phthalic anhydride in residue distillation collection tank (SP5).

The above samples to be analysed for components as described in Appendix B.

Due to continuous complications and maintenance on the residue distillation system since March 2000, trials as planned above could not be carried out successfully. Trials were also complicated by a raw material shortage experienced since February 2001. Due to the long downtime for maintenance

and raw material shortages experienced, it was decided to perform additional laboratory experiments during August 2001.

3.2 ADDITIONAL EXPERIMENTS – LABORATORY SCALE

It was observed in previous trials (Van Staden, 2001) that the residue formed a tar substance as the phthalic anhydride was being retrieved and the viscosity increased. The residue also collected around the anchor of the agitator, making agitation impossible. On cooling, the residue became rock-hard, making it labour intensive and difficult to remove out of the residue distillation kettle if it was not drained while still hot. However, hot draining of the residue also led to the possibility that lagging of the residue kettle could burn due to the very high temperature of the residue. Problems were also experienced with the reliability of the equipment. It was then decided to search for an additional treatment method, while maintenance was performed on the residue distillation system, to obtain a final residue that will be safe to handle and easy to dispose of.

The additional treatment method decided upon was to use Dicalite 4151 as treatment chemical (see specification sheet in Appendix C). Dicalite 4151 is normally used as a filter aid in the filtration of edible oils, sulphur, chrome solutions and industrial chemicals, but because of its inert characteristics, ability to handle high temperatures and availability, it was decided to test its compatibility with phthalic anhydride residue. The experimental tests performed in the laboratory are described in Section 3.2.1.

The laboratory experiments will give an indication of the optimum concentration of Dicalite 4151 to be used for plant scale experiments. (The plant scale experiments will aim to retrieve the phthalic anhydride out of the residue with conventional distillation after treatment with Dicalite 4151. If successful, the environmental and safety issues regarding the draining of hot phthalic anhydride residue will be addressed.)

3.2.1 Equipment for the laboratory scale experiments

The equipment used in the laboratory experiments (set-up illustrated in Figures 3.2 and 3.3) is as follows:

- pestle and mortar,
- 200 ml three-neck glass round ball flask,
- spatula,
- funnel to load phthalic anhydride residue and Dicalite 4151 into glass round ball flask,
- Hydolph mechanical agitator to agitate phthalic anhydride residue mixture at a rate of 1 revolution per second,
- hot plate with settings for magnetic stirrer and temperature control,
- oil bath of which the temperature is controlled at 155°C with a temperature controller,
- magnetic stirrer to keep hot oil mixed thoroughly to achieve a homogeneous temperature,
- water-cooled glass condenser,
- chiller for cooling of condenser at a temperature of 10°C,
- cold trap to protect pump from condensable vapours released by the system under vacuum,
- vacuum pump, and
- heating gun.

3.2.2 Laboratory scale experimental procedure

The experimental procedure to be used is as follows:

- Collect phthalic anhydride residue from the main distillation kettle and reduce to a powder with pestle and mortar for the laboratory tests (to achieve molten state quicker).
- Weigh off 30 g of powdered phthalic anhydride in a beaker and note the exact weight.

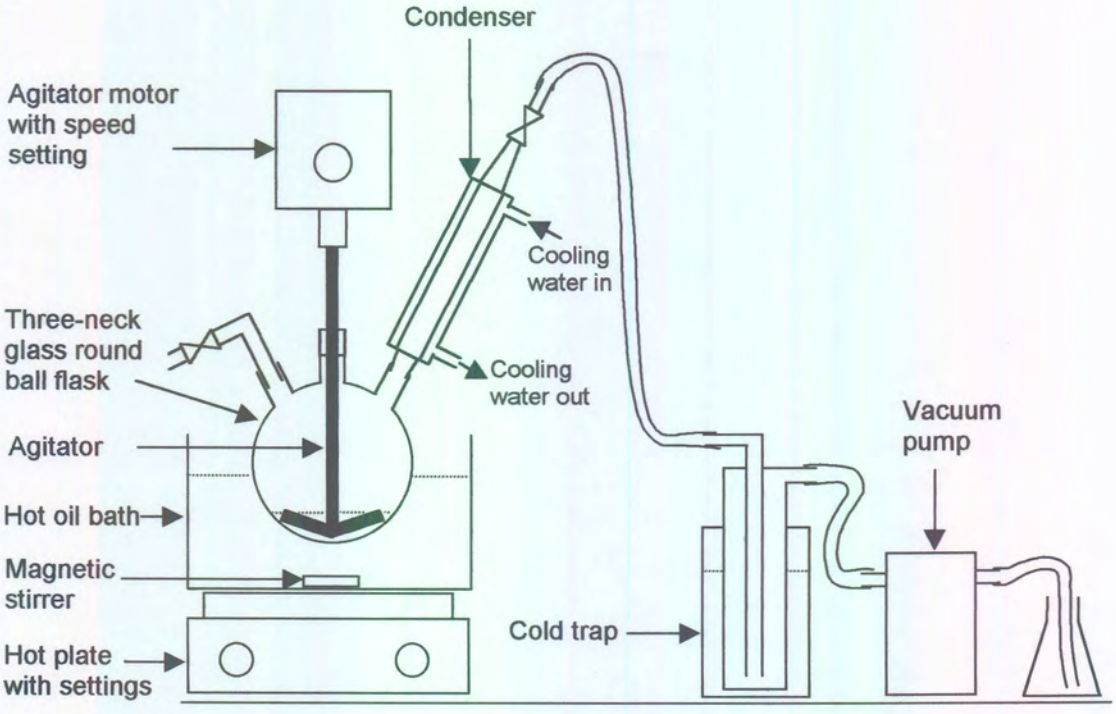


Figure 3.2 Schematic representation of experimental set-up of laboratory scale experiments.

Figure 3.3 Experimental set-up in laboratory.

- Switch the agitator on at a speed of 1 revolution per second. Transfer the measured powdered phthalic anhydride residue to the flask using a funnel.
- Switch the agitator off after the powdered phthalic anhydride residue has been transferred.
- Immerse the flask and its contents in a pre-heated hot oil bath with a temperature of 155°C. (The melting point of phthalic anhydride residue is close to that of pure phthalic anhydride, which is 130,8°C.)
- Heat the phthalic anhydride residue for approximately 60 minutes until melted. Note the time to achieve the molten state.
- Weigh off an amount of Dicalite 4151 in a beaker according to the concentration required and note the exact weight.
- Once the phthalic anhydride residue has melted, switch the agitator on and transfer the Dicalite 4151 that was weighed slowly into the flask using a funnel.
- Agitate the mixture for 10 to 15 minutes. To ensure homogeneity of the mixture, switch the agitator off and scrape the sides of the flask with a spatula where agitation is insufficient. Thereafter, continue with agitation.
- Apply vacuum (of 46 mbar) for 2 hours until most of the phthalic anhydride product sublimates out of the mixture. Scrape the sides of the flask where agitation is insufficient every 15 minutes to ensure thorough agitation (agitator and vacuum must be switched off before scraping). Phthalic anhydride needles that collect around the agitator shaft and the sides of the flask must be heated with a heating gun to aid in sublimation and removal of the phthalic anhydride.
- Stop the vacuum pump after the 2 hour period when most of the phthalic anhydride is retrieved out of the mixture. Note the time required for removal of phthalic anhydride.
- Remove the flask from the hot oil bath while agitating.
- Switch the stirrer off after 15 minutes of agitation.
- Transfer the final residue mixture to a sample bottle for examination.

3.3 ADDITIONAL EXPERIMENTS - PLANT SCALE

The experimental method used for operating the residue distillation system is as described by the standard operating procedures of the company for the plant.

As described in Section 2.5, crude phthalic anhydride is transferred batch-wise to one of three pre-treatment kettles, where it is heated to a temperature of 220°C to convert phthalic acid to phthalic anhydride. After heat treatment, sodium carbonate is added in the pre-treatment kettle to polymerise any naphthaquinones in the crude phthalic anhydride to a high boiling residue.

Low boiling constituents such as maleic anhydride and benzoic acid are then removed with distillation. The bottom product is transferred to one of two main distillation kettles from which pure phthalic anhydride are recovered with further distillation and collected in the pure phthalic anhydride storage tanks.

To perform the treatment of the phthalic anhydride residue with Dicalite 4151, a certain amount of Dicalite 4151 (as determined from the laboratory scale experiments) will be preloaded into the residue distillation kettle through the top manhole of the kettle. The weight of Dicalite 4151 loaded will be noted. The residue distillation kettle will be heated with an oil flow of 8 000 kg/h (via the oil flow control system, FIC71501) to obtain a temperature in the residue distillation kettle of 280°C, before transferring the residue from the main distillation kettle. The residue distillation kettle agitator will be switched on for agitation of the loaded Dicalite 4151 to ensure sufficient heat transfer. (Heating of the residue distillation kettle is crucial to prevent the solidification of the phthalic anhydride residue in the transfer lines and residue distillation kettle during transfer.)

After a sufficiently high temperature (170°C) has been reached in the residue distillation kettle, transfer of a batch residue from the main distillation kettle can be commenced with. Pressure is applied in the relevant main distillation kettle with nitrogen to transfer the residue to the residue distillation kettle. The

dip valve on the residue distillation kettle will be kept open to ensure that there is no pressure build-up of the system. When transfer has been completed, the phthalic anhydride residue/Dicalite 4151 mixture must be agitated thoroughly for 30 minutes. The residue distillation collection tank inlet valve will then be opened and a 100 % vacuum pressure applied to the residue distillation system via the residue distillation vacuum jet valve (HIC71801).

Distillation is monitored with the flow indicator on the line connecting the residue distillation dephlegmator with the residue distillation collection tank. When distillation is complete, the residue distillation vacuum jet valve (HIC71801) is closed. Completion of the distillation is indicated by monitoring the amount of phthalic anhydride seen through the flow indicator beneath the residue distillation dephlegmator. Closing of the heat transfer oil inlet valve (FIC71501) stops heat transfer to the residue distillation kettle. While the residue distillation kettle is cooling down, the residue distillation kettle agitator will continue running until a temperature of 100°C is achieved. The agitator will then be stopped and the bottom flap valve opened. The agitator will be started again and the residue discharged into a disposal trolley.

CHAPTER 4
Results and discussion

4.1 EXISTING PLANT

Experiments to determine optimum distillation conditions were delayed due to equipment failures of the residue distillation system and raw material shortages. However, some tests were performed under 100% vacuum and maximum oil flow of 8 000 kg/h to determine whether phthalic anhydride product could be removed. Despite long batch times of almost 30 hours (due to heat transfer and vacuum problems), the tests proved to be successful. Analysis of the phthalic anhydride residue after distillation showed no traces of product (see Appendix E).

No process data could be collected due to the mechanical problems that were experienced and the non-optimal conditions of the system. It is, however, important to note that the distillation of the phthalic anhydride out of the residue could be achieved as first step to the investigation. The residue that remained in the residue distillation kettle was problematic to retrieve since it solidified to a rock-hard substance once cooled down. The residue had to be removed manually out of the residue distillation kettle. Pieces of the residue obtained are shown in Figure 4.1.

Figure 4.1 Sample of phthalic anhydride residue after distillation.

Most of the tests performed were handicapped by equipment failures and only resumed when maintenance had been completed. While maintenance was performed to improve the reliability and operability of the residue distillation system, it was decided to search for other possibilities to improve the final form of the residue to a substance that is safe to handle and easy to dispose of. The results of these experiments are reported and discussed in the following sections.

4.2 ADDITIONAL EXPERIMENTS - LABORATORY SCALE

The experimental method, as described in Section 3.4.1, was used to determine the optimum concentration of Dicalite 4151 required to phthalic anhydride residue to ensure a powdered residue mixture at the end of the treatment. Four sets of experiments were performed.

In Experiment A, the phthalic anhydride residue (composition shown in Appendix D) was melted and 0,3 kg Dicalite 4151 was added per kg of phthalic anhydride residue. The variables used during this experiment are shown in Table 4.1 (unprocessed data is shown in Appendix F). The results of these experiments are shown in Table 4.2 and illustrated in Figure 4.2.

Table 4.1 Monitored variables of Experiment A.

Variable \ Experiment		A1	A2	A3
Concentration (kg Dicalite 4151 per kg phthalic anhydride residue)		0,2997	0,3008	0,2997
Time (minutes)	Phthalic anhydride residue melted	65	65	67
	Agitation time before applying vacuum	10	10	8
	Vacuum application	90	110	217
	Cooling and agitation after treatment	15	15	15

It was found that although some of the phthalic anhydride needles were extracted out of the phthalic anhydride mixture with the application of vacuum, large

amounts collected around the shaft of the agitator. A heating gun was used to sublimate the phthalic anhydride crystals. To ensure the homogeneity of the mixture, a spatula was also used to scrape the bottom of the glass round ball flask where agitation was insufficient.

It was found that on retrieving the final residue mixture out of the flask, very little of the residue stuck to its sides.

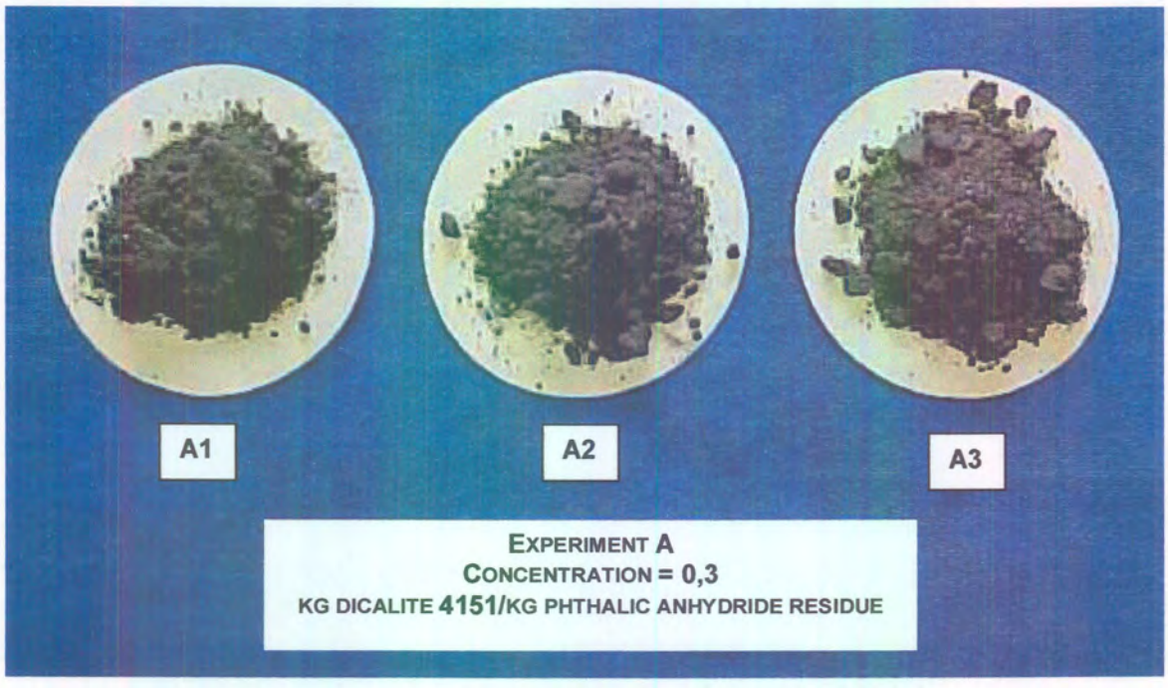


Figure 4.2 Final phthalic anhydride residue after treatment with Dicalite 4151 (Experiment A).

In Experiment B, the phthalic anhydride residue (composition shown in Appendix D) was melted and 0,2 kg Dicalite 4151 was added per kg of phthalic anhydride residue. The variables used during this experiment are shown in Table 4.3. The results of this experiment are shown in Table 4.2 and illustrated in Figure 4.3.

The same result was achieved as in Experiment A. The mixture was kept homogeneous by scraping the insufficient agitated parts of the flask with a spatula. There remained a small amount of residue stuck to the bottom of the flask.

Table 4.2 Results of laboratory scale experiments.

Experiment Number	Concentration (kg Dicalite 4151 per kg phthalic anhydride residue)	Result
Experiment A – 0,3 kg Dicalite 4151/kg phthalic anhydride residue		
A1	0,300	Powder with lumps (see Figure 4.2).
A2	0,301	Powder with lumps (see Figure 4.2).
A3	0,300	Powder with lumps (see Figure 4.2).
Experiment B – 0,2 kg Dicalite 4151/kg phthalic anhydride residue		
B1	0,200	Powder with lumps (see Figure 4.3).
B2	0,199	Powder with lumps (see Figure 4.3).
B3	0,201	Powder with lumps (see Figure 4.3).
Experiment C – 0,1 kg Dicalite 4151/kg phthalic anhydride residue		
C1	0,101	Residue mixture stuck to sides of flask and could not be retrieved.
Experiment D – 0,15 kg Dicalite 4151/kg phthalic anhydride residue		
D1	0,150	Small rocks (see Figure 4.4).
D2	0,150	Small rocks (see Figure 4.4).
D3	0,150	Small rocks (see Figure 4.4).

Table 4.3 Monitored variables of Experiment B.

Variable \ Experiment		B1	B2	B3
Concentration (kg Dicalite 4151 per kg phthalic anhydride residue)		0,200	0,199	0,201
Time (minutes)	Phthalic anhydride residue melted	40	60	50
	Agitation time before applying vacuum	15	10	10
	Vacuum application	30	40	75
	Cooling and agitation after treatment	20	15	15

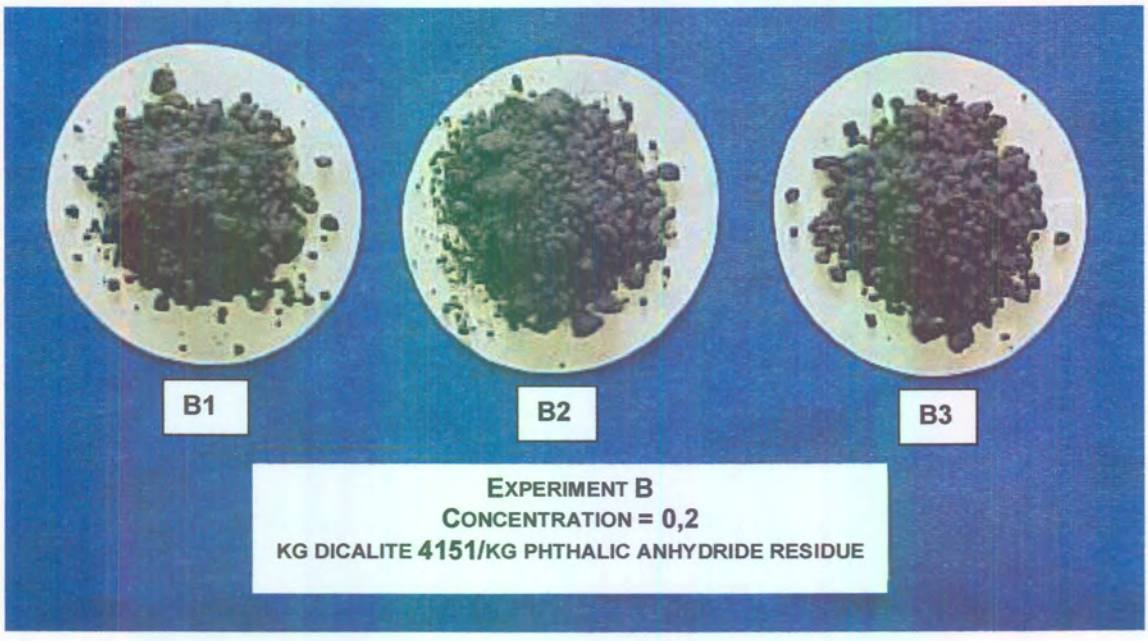


Figure 4.3 Final phthalic anhydride residue after treatment with Dicalite 4151 (Experiment B).

In Experiment C, the phthalic anhydride residue (composition shown in Appendix D) was melted and 0,1 kg Dicalite 4151 was added per kg of phthalic anhydride residue. The variables used in this experiment are shown in Table 4.4. The results of this experiment are shown in Table 4.2.

Table 4.4 Monitored variables of Experiment C.

Variable \ Experiment		C1
Concentration (kg Dicalite 4151 per kg phthalic anhydride residue)		0,1014
Time (minutes)	Phthalic anhydride residue melted	61
	Agitation time before applying vacuum	10
	Vacuum application	110
	Cooling and agitation after treatment	15

The phthalic anhydride residue/Dicalite 4151 mixture was tarry when it was scraped with a spatula to stir the insufficient agitated parts of the flask. On cooling after the vacuum application was stopped, the mixture became hard and could not be retrieved, since it stuck to the bottom of the flask. It was decided to discard further experiments with this concentration, but to perform more experiments (Experiment D) with a concentration of 0,15 kg Dicalite 4151/kg phthalic anhydride residue.

In Experiment D, the phthalic anhydride residue (composition shown in Appendix D) was melted and 0,15 kg Dicalite 4151 was added per kg of phthalic anhydride residue. The variables used in this experiment are shown in Table 4.5. The results of this experiment are shown in Table 4.2 and illustrated in Figure 4.4.

Table 4.5 Monitored variables of Experiment D.

Variable \ Experiment		D1	D2	D3
Concentration (kg Dicalite 4151 per kg phthalic anhydride residue)		0,150	0,150	0,150
Time (minutes)	Phthalic anhydride residue melted	55	60	60
	Agitation time before applying vacuum	10	10	10
	Vacuum application	60	65	120
	Cooling and agitation after treatment	10	10	10

During the application of vacuum to retrieve phthalic anhydride product, it was noted that the residue mixture collected around the anchor of the agitator. It was relatively easy to scrape the parts of the bottom of the flask where agitation was insufficient. On cooling, small rocks formed (see Figure 4.4), which could be easily retrieved from the flask. There was, however, an amount of residue that stuck to the bottom of the flask.

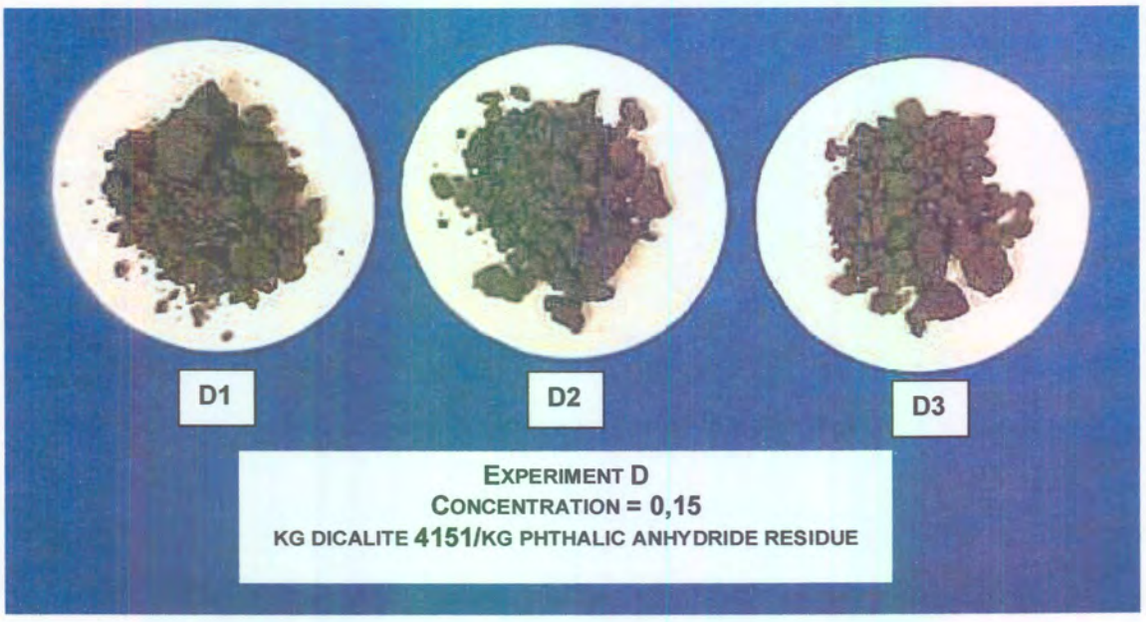


Figure 4.4 Final phthalic anhydride residue after treatment with Dicalite 4151 (Experiment D).

4.3 ADDITIONAL EXPERIMENTS - PLANT SCALE

The experimental method, as described in Section 3.3, was used to perform trials on plant scale to determine the amount of Dicalite 4151 to be used to achieve optimal distillation of phthalic anhydride out of the residue and to produce a residue that is safe to handle and easy to dispose of.

In Experiment E, the residue distillation kettle was preloaded with Dicalite 4151 (see Table G.1, Appendix G). The residue distillation kettle was heated to a final temperature of 145,2°C via an oil flowrate of 7 200 kg/h at an oil temperature of 300°C.

Phthalic anhydride residue was transferred from the main distillation kettle to the residue distillation kettle to achieve a concentration of 0,361 kg Dicalite 4151 per kg of phthalic anhydride residue. Monitored plant variables are shown in Table 4.6 (unprocessed data is shown in Appendix G). The temperature of the phthalic anhydride residue during transfer was 263,5°C.

Table 4.6 Monitored variables of Experiment E.

Variable \ Experiment		E
Concentration (kg Dicalite 4151 per kg phthalic anhydride residue)		0,361
Time (hours)	Residue distillation kettle at steady state temperature	20,5
	Agitation time before applying vacuum	4
	Vacuum application	1
	Cooling and agitation after treatment	18

After transferring the phthalic anhydride residue, the mixture was agitated for 45 minutes to achieve thorough mixing of the filter aid and residue. Problems were experienced with the agitator and were addressed. See Table 4.6 for the time accorded to agitation, which includes the time that the agitator was worked on. After agitation, a manual level measurement of the residue distillation kettle was performed, which also served the purpose of determining the state of the residue mixture. A powder was found on the measuring stick.

Vacuum was then applied to the residue distillation system at a maximum pressure of 11 kPaa and the temperature was raised from 170,6°C to a maximum temperature of 218°C. At this temperature, product seemed to distil off easily (as observed in the sight glass). However, the operation was stopped when blockages were found in the product pipeline between the residue distillation dephlegmator and residue distillation collection tank. The vacuum application was stopped and the agitator kept running until maintenance could be performed to unblock the pipeline. The residue distillation kettle was kept at a temperature of 170,2°C.

After maintenance was performed (18 hours after the vacuum was released), another level measurement of the residue distillation kettle was taken. This time a tarry residue remained on the measuring stick. This could be due to the long agitation time and high temperature in the residue distillation kettle resulting in the

phthalic anhydride residue mixture becoming tar-like again. It was decided to dispose of the mixture and recheck the residue distillation system for more blockages.

The residue mixture was dropped out of the residue distillation kettle into a disposal trolley while still hot (temperature above 170°C). During this time the residue distillation agitator was kept running. The appearance of the residue was very viscous. The disposed residue mixture was left to cool down and on closer inspection, it was found that the residue mixture was lumpy and hard. This was also the case when the inside of the residue distillation kettle was inspected where a small amount of rock-like remains could be retrieved easily. See Figure 4.5 for illustration of residue after treatment with Dicalite 4151 and distillation. A sample of the residue was taken before transfer to the residue distillation kettle. No other samples were collected due to the curtailment of the experiment.

Figure 4.5 Final phthalic anhydride residue after treatment with Dicalite 4151 (Experiment E).

In Experiment F, the residue distillation kettle was preloaded with Dicalite 4151 (see Table G.2, Appendix G) and the same operating procedure followed as for

Experiment E. The residue distillation kettle was heated to a final temperature of 132,5°C via an oil flowrate of 8 147 kg/h at an oil temperature of 300°C.

Phthalic anhydride residue was transferred from the main distillation kettle to the residue distillation kettle to achieve a concentration of 0,192 kg Dicalite 4151 per kg of phthalic anhydride residue. Plant variables are shown in Table 4.7 (unprocessed data is shown in Appendix G). The temperature of the phthalic anhydride residue during transfer was 283,2°C.

Table 4.7 Monitored variables of Experiment F.

Variable \ Experiment		F
Concentration (kg Dicalite 4151 per kg phthalic anhydride residue)		0,192
Time (hours)	Residue distillation kettle at steady state temperature	22
	Agitation time before applying vacuum	0,8
	Vacuum application	8,9
	Cooling and agitation after treatment	27

After transferring the batch, the mixture was agitated for 50 minutes to achieve thorough mixing of the filter aid and residue. A vacuum of 12,2 kPaa was applied and the temperature of the residue distillation kettle was raised from 177,8°C to a maximum of 220°C. At this temperature, product distilled off at a rate of between 0,637 and 3,104 kg/minute (see Appendix G for rate at which distillation took place). The amount of phthalic anhydride recovered was 1 186,836 kg, which took approximately 10 hours to collect.

A manual level measurement of the residue distillation kettle was performed, which once again also provided an indication of the state of the residue mixture, and a tarry residue remained on the measuring stick, similar to Experiment E. There was still some phthalic anhydride desublimating from the residue mixture on the measuring stick.

The top manhole of the residue distillation kettle was opened while the kettle was cooling down. The residue mixture had a thick, tar-like appearance and took 27 hours to cool down from 171°C to 108°C. The residue mixture was disposed into a disposal trolley and was thick and lumpy of appearance (see Figure 4.6). It crumbled while it was still hot to form rock-hard lumps when cooled. An amount of phthalic anhydride remained in the residue mixture, but the fumes were less than with the original draining procedure from the main distillation kettle. The final residue did not compare well with the results achieved in the laboratory with the same concentration.

Figure 4.6 Final phthalic anhydride residue after treatment with Dicalite 4151 (Experiment F).

Samples of the residue before treatment (SP3), residue after treatment and distillation (SP4), and product collected in the residue distillation collection tank (SP5) were analysed for phthalic anhydride content to determine the percentage recovery (see results in Appendix H) with Equation 3.1. The calculated recovery of phthalic anhydride was 97,69%.

Due to the results obtained in Experiment F it was decided to increase the ratio of Dicalite 4151 to phthalic anhydride residue. A smaller amount of phthalic anhydride residue was subsequently loaded to the residue distillation kettle in Experiment G (see Table G.3, Appendix G). The same operating procedure was followed as for Experiment E. The residue distillation kettle was heated to a final temperature of 145,4°C via an oil flowrate of 8 250,4 kg/h at an oil temperature of 300°C.

Phthalic anhydride residue was transferred from the main distillation kettle to the residue distillation kettle to achieve a concentration of 0,275 kg Dicalite 4151 per kg of phthalic anhydride residue. Plant variables are shown in Table 4.8 (unprocessed data is shown in Appendix G). The temperature of the phthalic anhydride residue during transfer was 265,2°C.

Table 4.8 Monitored variables of Experiment G.

Variable \ **Experiment**		**G**
Concentration (kg Dicalite 4151 per kg phthalic anhydride residue)		0,275
Time (hours)	Residue distillation kettle at steady state temperature	30
	Agitation time before applying vacuum	2,8
	Vacuum application	n/a
	Cooling and agitation after treatment	n/a

After transferring the batch, the mixture was agitated for 170 minutes to achieve thorough mixing of the filter aid and residue. A manual level measurement of the residue distillation kettle was taken, which simultaneously also gave an indication of the state of the residue mixture and a powder remained on the measuring stick.

A vacuum of 18,2 kPaa was applied (vacuum loss was apparent when compared to Experiment F) and the temperature of the residue distillation kettle was raised from 165,1°C to a maximum of 198°C. However, in contrast to Experiment F, no

product was distilled off. Inspection of the heat transfer system, showed that heat transfer to the vapour line between the residue distillation kettle and residue distillation dephlegmator was insufficient. Due to this problem, no distillation took place. The problem was addressed and vacuum was applied again. However, attempts to distil were still unsuccessful and it was decided to dispose of the residue mixture into a disposal trolley.

The top manhole of the residue distillation kettle was opened while the kettle was cooling down. The residue mixture had a thick, dry appearance. On disposal, the temperature of the residue distillation kettle was 167,3°C (due to the long cooling time experienced in Experiment F, it was decided to dispose of the residue mixture at a higher temperature). On disposal of the residue mixture, phthalic anhydride fumes were released to the atmosphere as was the case with normal draining of the main distillation kettle.

On closer inspection of the disposed residue, it was found that the residue mixture was powder-like with small lumps. See Figure 4.7 for illustration of residue after treatment with Dicalite 4151 and distillation.

Samples of the residue before treatment (SP3), residue after treatment and distillation (SP4), and product collected in the residue distillation collection tank (SP5) were analysed for phthalic anhydride content. The phthalic anhydride content decreased with 32,9% due to desublimation that took place during the draining procedure (see Appendix H).

Although no phthalic anhydride had been recovered it was proved that with the addition of Dicalite 4151 at a concentration of 0,275 kg Dicalite 4151 per kg phthalic anhydride residue, a powder can be formed as in the laboratory experiments.

Due to the loss of vacuum experienced in Experiment G, it was decided to perform vacuum tests and perform necessary maintenance to ensure that this problem would not affect further experiments.

Figure 4.7 Final phthalic anhydride residue after treatment with Dicalite 4151 (Experiment G).

In Experiment H, the residue distillation kettle was preloaded with Dicalite 4151 (see Table G.3, Appendix G) and the same operating procedure followed as for Experiment E. The residue distillation kettle was heated to a final temperature of 124°C via an oil flowrate of 7 904,2 kg/h at an oil temperature of 300°C.

Transfer of the phthalic anhydride residue was delayed due to problems experienced with production in the main distillation section of the plant.

Phthalic anhydride residue was transferred from the main distillation kettle to the residue distillation kettle to achieve a concentration of 0,302 kg Dicalite 4151 per kg of phthalic anhydride residue. Plant variables are shown in Table 4.9 (unprocessed data is shown in Appendix G). The temperature of the phthalic anhydride residue during transfer was 277°C.

Table 4.9 Monitored variables of Experiment H.

Variable \ Experiment		H
Concentration (kg Dicalite 4151 per kg phthalic anhydride residue)		0,302
Time (hours)	Residue distillation kettle at steady state temperature	118,9
	Agitation time before applying vacuum	0,9
	Vacuum application	intermittently
	Cooling and agitation after treatment	n/a

After transferring the batch, the mixture was agitated for 55 minutes to achieve thorough mixing of the filter aid and residue. A manual level measurement of the residue distillation kettle was taken. As before, this action also provided an indication of the state of the residue mixture with a powder present on the measuring stick.

A vacuum of 9,8 kPaa was applied and the temperature of the residue distillation kettle was raised from 171,1°C to 209,4°C. At this temperature, product distilled off at a rate of between 0,112 and 1,011 kg/minute (see Appendix G for rate at which distillation took place). The amount of phthalic anhydride recovered was 425,064 kg, which took approximately 48 hours to collect.

However, distillation had to be stopped at intervals when the rate of distillation became too slow (inspection of the sight glass showed that product was only dripping). Vacuum application was stopped and the residue distillation kettle heated until a steady state temperature was reached (between 168,7°C and 173°C). The time to distil the product in Experiment H therefore took 38 hours longer than for Experiment F. This could be due to a higher concentration of Dicalite 4151 used in Experiment H than in Experiment F (compare 0,302 to 0,192 kg Dicalite 4151 per kg phthalic anhydride residue).

The top manhole of the residue distillation kettle was opened while the kettle was cooling down. The residue mixture appeared dry. The temperature of the residue

distillation kettle was 147,3°C before disposal (due to the long cooling time experienced in Experiment F, it was decided to dispose of the residue mixture at a higher temperature, similar to Experiment G). Although there were still phthalic anhydride fumes on disposal of the residue mixture, it was much less than for a normal draining of a main distillation kettle. Residue mixture powder (see Figure 4.8 for illustration of residue after treatment with Dicalite 4151 and distillation) flowed out of the residue distillation kettle with the agitator running. The residue distillation kettle was emptied in 20 minutes.

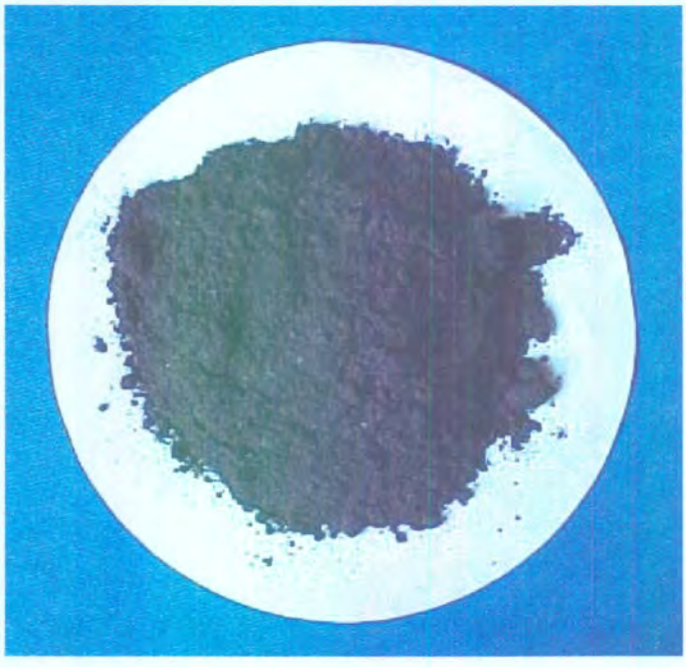


Figure 4.8 Final phthalic anhydride residue after treatment with Dicalite 4151 (Experiment H).

Samples of the residue before treatment (SP3), residue after treatment and distillation (SP4), and product collected in the residue distillation collection tank (SP5) were analysed for phthalic anhydride content to determine the percentage recovery (see results in Appendix H) with Equation 3.1. The calculated recovery of phthalic anhydride was 53,95%.

In Experiment I, it was decided to add Dicalite 4151 to the phthalic anhydride residue after transfer and distillation in the residue distillation kettle to determine

whether distillation will take place at a faster rate. The same operating procedure for distillation was followed as for Experiment E, with the only difference of adding the Dicalite 4151 at a later stage. The residue distillation kettle was heated to a final temperature of 124°C via an oil flowrate of 7 904,2 kg/h at an oil temperature of 300°C.

Phthalic anhydride residue was transferred to the residue distillation kettle. Plant variables are shown in Table 4.10 (unprocessed data is shown in Appendix G). The temperature of the phthalic anhydride residue during transfer was 278°C.

Table 4.10 Monitored variables of Experiment I.

Variable \ **Experiment**		**I**
Concentration (kg Dicalite 4151 per kg phthalic anhydride residue)		0,321
Time (hours)	Residue distillation kettle at steady state temperature	5,3
	Agitation time before applying vacuum	Immediately
	Vacuum application	Intermittently (see Appendix G)
	Cooling and agitation after treatment	35,5

A vacuum of 10,4 kPaa was applied and the temperature of the residue distillation kettle raised from 200°C to a maximum of 208°C. At this temperature, product distilled off at a rate of between 0,349 and 1,815 kg/minute (see Appendix G for rate at which distillation took place). The amount of phthalic anhydride recovered was 384,468 kg, which took approximately 36 hours.

However, distillation had to be stopped at intervals when the rate of distillation became too slow (inspection of the sight glass showed that product was only dripping). Vacuum application was stopped and the residue distillation kettle heated until a steady state temperature was reached (between 168,3°C and 180,2°C).

Distillation became very slow and it was decided to then add the Dicalite 4151 through the top manhole of the residue distillation kettle to achieve a concentration of 0,321 kg Dicalite 4151 per kg phthalic anhydride.

After loading the Dicalite 4151, the mixture was agitated for 115 minutes to achieve thorough mixing of the filter aid and residue. A vacuum of 12,2 kPaa was applied again. After approximately one hour, distillation started and maximum temperatures in the residue distillation kettle of up to 220,3°C were reached (an indication of good distillation of phthalic anhydride). At this temperature, product distilled off at a rate of 0,972 kg/minute (see Appendix G for rate at which distillation took place). The amount of phthalic recovered during the second distillation period of 4,6 hours was 288,948 kg. The total amount of phthalic anhydride recovered was 673,416 kg, which took approximately 41 hours in total. With Experiment I, an actual printout from the plant's control parameters during the experiment is shown in Appendix I.

A manual level measurement of the residue distillation kettle was performed. Similar to Experiment H, a powder remained on the measuring stick.

This experiment indicates that distillation of the raw phthalic anhydride residue takes place at a higher rate when Dicalite 4151 is preloaded (compare with Experiment H). It was also shown that with the addition of Dicalite 4151, the rate of distillation increases (also see rate of distillation of Experiment F). This should be taken into account when deciding on a procedure for the addition of Dicalite 4151 to the residue.
The oil flow to the residue distillation kettle was stopped and the residue distillation kettle cooled down to a temperature of 71,7°C before disposal. The residue mixture powder (see Figure 4.9 for illustration of residue after treatment with Dicalite 4151 and distillation) flowed out of the residue distillation kettle with the agitator running. The residue distillation kettle was emptied in approximately 20 minutes.

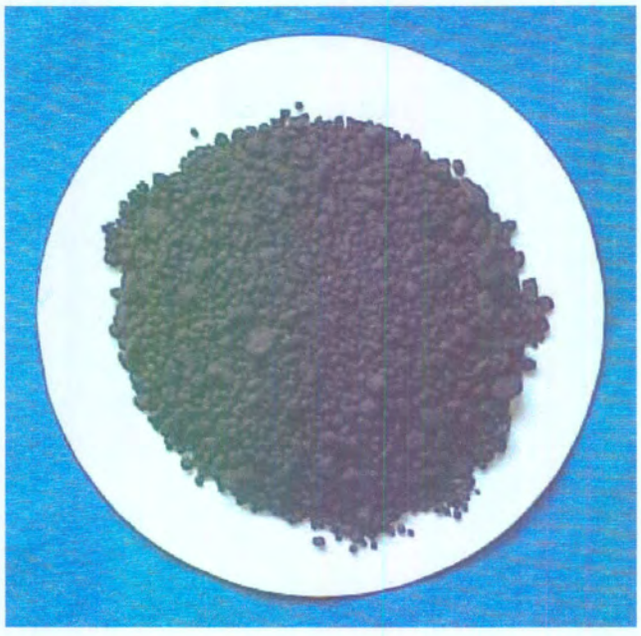


Figure 4.9 Final phthalic anhydride residue after treatment with Dicalite 4151 (Experiment I).

Figure 4.10 Residue mixture released into a disposal trolley after distillation and treatment with Dicalite 4151 (Experiment I).

On disposal of the residue mixture, no phthalic anhydride fumes were released to the atmosphere. However, there was a fair amount of dust present from releasing the residue powder into the disposal trolley (see Figure 4.10).

Samples of the residue before treatment (SP3), residue after treatment and distillation (SP4), and product collected in the residue distillation collection tank (SP5) were analysed for phthalic anhydride content to determine the percentage recovery (see results in Appendix H) with Equation 3.1. The calculated recovery of phthalic anhydride was 81,97%, a higher recovery than for Experiment H, but lower than the recovery of Experiment F.

CHAPTER 5
Conclusions and recommendations

Treatment of phthalic anhydride residue with distillation and addition of Dicalite 4151 in the residue distillation kettle improved the handling and disposal of the hot, liquid phthalic anhydride residue previously drained directly from the main distillation kettles.

With the laboratory experiments it was found that a concentration of 0,2 kg Dicalite 4151 per kg phthalic anhydride residue was sufficient to produce a powdered residue. However, the use of a similar concentration during the plant scale experiments (Experiment F) did not produce similar results.

Increasing the ratio of Dicalite 4151 to phthalic anhydride for experiments G, H and I have been successful in transforming the residue liquid to a powder on plant scale. However, the increased ratio of Dicalite 4151 to phthalic anhydride residue decreased the recovery of phthalic anhydride. In Experiment F (with a concentration of 0,19 kg Dicalite 4151 per kg phthalic anhydride residue), the rate of distillation (between 0,637 and 3,104 kg/minute) was higher than experiments H and I (with concentrations of 0,302 and 0,321 kg Dicalite 4151 per kg phthalic anhydride residue respectively), where the distillation rates varied between 0,112 and 1,815 kg/minute. However, in Experiment I the Dicalite 4151 was added at a later stage in the experiment, which increased the distillation rate. It is recommended that this observation be verified with more trials on the plant. This observation could be used to shorten distillation batch times, thereby preventing the bottlenecking of the distillation process.

During the plant experiments performed, it was confirmed that vacuum application is crucial to the successful distillation of phthalic anhydride. The addition of Dicalite 4151 in the plant experiments took place through the top manhole of the residue distillation kettle. The use of this manhole led to vacuum loss when the manhole cover was not fastened well enough after loading the Dicalite 4151. It is recommended that this manhole should not be used for addition, therefore to

reduce the risk of vacuum loss. A modification to load the Dicalite 4151 through another available porthole on the residue distillation kettle and equipping it with a funnel and valve should be considered.

During the plant scale experiments, heat transfer to the residue distillation kettle was sometimes problematic due to an undersized burner system. This should be addressed to ensure sufficient heat transfer, which is critical for successful distillation of phthalic anhydride in the residue.

The physical state of the hot liquid phthalic anhydride residue after distillation and addition of Dicalite 4151 in the residue distillation kettle has been altered to a powdered form. However, the powdered phthalic anhydride residue produces a dust when drained into the disposal trolley. This problem can be addressed by designing a cylindrical chute to fit over the bottom flap valve of the residue distillation kettle to reduce the amount of dust when discharging the residue.

With substantial changes made to the residue, the possibility exists that the residue now resides under a lower hazard rating. It is recommended that the residue's hazard classification be revisited. This could result in a lower hazard rating with possible savings in the final disposal of the residue.

Finally, similar residues can be problematic to handle and dispose of in other industries as well. The results obtained during these laboratory experiments and plant trials with the use of Dicalite 4151 (or other filter aids) should be tested with residues formed in other industries to determine whether the same effect can be achieved to result in improved handling and disposal of relevant residues.

References

ACKERMANN, P. (1965) Recover PA from distillation residue, *Hydrocarbon Processing*, 44 (11), November, 291 – 292.

AUSTIN, G.T. (1984) *Shreve's Chemical Process Industries*, 5th edition, New York: McGraw-Hill International Editions.

BARRON, C., SAKUMA, Y. and SCHELLENBERG, T. (1995) *Chemical Economics Handbook*, CEH Marketing Research Report – Phthalic Anhydride, [SI]: SRI International.

BS 3773 (1964) *Specification for Phthalic Anhydride*, BSI, London.

CEH, *Chemical economics handbook*, Abstract of CEH report Phthalic anhydride Internet: http://www.ceh.sric.sri.com/Public/Reports/687.5000/Abstract.html. Accessed: 10 April 2000.

CSDS (1956) *CHEMICAL SAFETY DATA SHEET SD-61: Phthalic anhydride,* Washington DC: MCA.

CS, (1995) *CHEM SYSTEMS Phthalic anhydride 93-3*, May, New York: Chem Systems Inc.

CPSC (1998) *Releases Study on Phthalates in Teethers, Rattles and Other Children's Products*, Release #99-031, 2 December. *Internet*: http://www.kidsource.com/CPSC/phthalates.study.cpsc.html. Accessed 30 August 2000.

DAVEY, W.L.E. (1985) PA Yields: Briefing Note, *PED, NCP internal confidential report no. WLED/vf*, Johannesburg, South Africa.

DONALDSON, N. (1958) *The Chemistry and Technology of Naphthalene Compounds*, London: Edward Arnold (Publishers) Ltd.

ECPI (1999) *ECPI technical papers – The use of phthalate plasticisers in soft PVC toys*, May. *Internet*: http://www.ecpi.org/technical-papers/9905-the-use-of-phthalates.html. Accessed: 30 August 2000.

ELVERS, B., HAWKINS, S. and SCHULZ, G. (1992) *Ullman's Encyclopedia of Industrial Chemistry*, (A20), 5th completely revised edition, New York: VCH.

EPA (1994a) *Pollution Prevention and Toxics, Phthalic anhydride fact sheet*, November, CAS no. 85-44-9, EPA749-F-95-016, U.S. EPA:

Washington D.C., *Internet*: http://www.epa.gov/opptintr/chemfact/phtha-fs.txt. Accessed: 15 February 1999.

EPA (1994b) *Pollution Prevention and Toxics, Phthalic anhydride fact sheet: Support document (CAS no. 85-44-9)*, December, U.S. EPA 749-F-95F016a, *Internet:* http://www.db.rtk.net/E16043T676. Accessed: 30 August 2000.

JEFFERY, G.H., BASSETT, J., MENDHAM, J. AND DENNEY, R.C. (1989) *Vogel's Textbook of Quantitative Chemical Analysis*, 5th edition, London: Longman Scientific & Technical.

KROSCHWITZ, J.I. and HOWE-GRANT, M. (1996) *Encyclopedia of Chemical Technology*, (18), 4th edition, New York: John Wiley & Sons Inc.

LLOYD, D.D. (1983) PA Catalysts, *PED, NCP internal confidential report no.* SDV.M.T.35A/1/DDL/gb, Johannesburg, South Africa.

LLOYD, D.D. (1985) Preliminary Report on H Gehrken's Visit, *PED, NCP internal confidential report no. PED.M.T.35A/1/DDL/ydup*, Johannesburg, South Africa.

McKETTA, J.J. AND CUNNINGHAM, W.A. (1991) *Encyclopedia of Chemical Processing and Design*, (36), *Phthalic anhydride.*, New York: Marcel Dekker Inc.

OCKERBLOOM (2000) *Mixed xylenes, orthoxylene, phthalic anhydride, 2-ethylhexanol & phthalates monthly business report* (145), 24 July, ME: Ockerbloom and Co., Inc.

OWENS, R. (2000) *Personal communication*, NCP, Johannesburg, South Africa.

PAVLOVICH, L.B., KARBAINOV, A.D., ALEKSEEVA, N.M. and PRUDKAI, P.A. (1997) Still bottoms from distillation of phthalic anhydride as a raw material for production of powder dyes, *Coke and Chemistry*, (1), 42 – 47.

PERRY, R.H. and GREEN, D. (1984) *Perry's Chemical Engineer's Handbook*, 6th edition, Singapore: McGraw-Hill Inc.

SABS 905 (1968) *Standard Specification for Phthalic Anhydride 6.5*, 8, Council of the South African Bureau of Standards.

SITTIG, M. (1979) *Hazards and Toxic Effects of Industrial Chemicals*, New Jersey: Noyes Data Corp.

SKOOG, DOUGLAS A. and LEARY, JAMES J. (1992) *Principles of Instrumental Analysis*, 4th edition, Saunders College Publishing.

TACK, P.F. (1988) Deactivation of Catalyst NXR in PA-3 Reactor, *PED, NCP internal confidential report no. T35A/1,* Johannesburg, South Africa.

TECNON (2000) *Monthly newsletter, orthoxylene phthalic anhydride* (260), 8th August, UK: Tecnon Consulting World Network.

TRUMAN, A.H. (1970) Batch distillation of Phthalic anhydride, *Chemical Engineering Progress*, 66 (3), March, 62 – 65.

VAN DER MERWE, D.E. (1989) PA Catalyst Order Plan, *PED, NCP internal confidential report no.* 507/89/c, Johannesburg, South Africa.

VAN DER MERWE, D.E. (1996) PA3 catalyst & PA distillation monitors, *PED, NCP internal confidential report no.* T.35/1, Johannesburg, South Africa.

VAN STADEN, K. (2001) PA Residue Progress Report, *PED, NCP internal confidential report no.* PED.M.T35/14c/60, Johannesburg, South Africa.

WUNSHC, I. (1987) Quotation catalyst NXD and NXR for phthalic anhydride, *PED, NCP internal confidential telefax no.* T35A/1, Johannesburg, South Africa.

APPENDIX A

Advantages and disadvantages of different reactor catalysts used

Table A.1 Advantages and disadvantages of the pellet and spherical type catalyst used on the phthalic anhydride plant (Lloyd, 1983 and Davey, 1985).

Pellet type catalyst	Spherical type catalyst
Advantages	
• 7 year life span, and • easy distillation of residue.	• 3 year life span, • 0,5 % residue, • no fouling of condensers, • lower pressure drop over catalyst bed, • higher naphthalene feed capacity, and • scrubbed tail gas resulted in the production of maleic anhydride and fumaric acid formation.
Disadvantages	
• 3,5 % residue formation, • fouling of condensers due to residue formation, and • tail gas can't be scrubbed.	• lower yield of product, and • difficult purification stage.

APPENDIX B

Analytical methods

Samples collected with the plant scale trials to be tested for the following components using the analytical methods described in Table B.1 and the references to these methods discussed in the following paragraphs:

- total acidity as phthalic acid (% m/m), as measure of phthalic anhydride present in residue,
- free acidity as phthalic acid by non-aqueous titration (%), as measure of phthalic anhydride in residue,
- maleic anhydride content (ppm),
- phthalimide content (% m/m),
- benzoic acid content (ppm),
- naphthaquinone content (ppm), to give a measure of how efficient the polymerisation reactions were in the pre-treatment of the crude phthalic anhydride,
- anthraquinone content (ppm),
- sodium content (% m/m), and
- sulphate content (ppm).

Table B.1 Analytical methods for determination of components in samples.

Parameter	Analytical Method
Total acidity as phthalic acid (% m/m)	MOA No 1.17.3.6.1
Free acidity as phthalic acid (% m/m)	MOA No 1.17.3.18
Maleic anhydride (ppm)	MOA No 1.17.3.8
Phthalimide (% m/m)	MOA No 1.17.3.5
Benzoic acid (ppm)	MOA No 1.17.3.5
Naphthaquinone (ppm)	MOA No 1.17.3.7.1
Anthraquinone (ppm)	MOA No 1.17.3.5
Ash %	MOA No 1.17.3.4
Sodium content (% m/m)	Inductively coupled plasma photometry
Sulphate (ppm)	MOA No QCM

MOA = Method of analysis

MOA No 1.17.3.6.1

Phthalic anhydride content is measured by titration and high-performance liquid chromatography (HPLC). The phthalic anhydride was titrated hot (above 60°C) with 1 N NaOH to a pink colour using phenolphthalein indicator (SABS 905, BS 3773).

MOA No 1.17.3.18

The percentage (m/m) free acidity as phthalic acid is determined by using a 10 g sample that is dissolved without heating using 150 cm^3 methyl ketone. Bromophenol blue indicator is used and the solution titrated with 0,1 M triemethyl solution until the colour changes from green to blue (BS 3773).

MOA No 1.17.3.8, 1.17.3.5 and 1.17.3.7.1

Maleic anhydride, benzoic acid, naphthalene, 1,4-naphthaquinone, anthraquinone and phthalimide content is determined by a gas chromatograph HP 5890 GC and an HP 3396 Integrator. Acetone HPLC grade and hexadecane internal standard solution is used as solvent.

MOA No 1.17.3.4 and ICPP

The ash content is determined from a sample of residue by burning it slowly in a platinum basin (SABS 905). It is then ignited in a furnace at 600 to 650°C until all the carbonaceous matter has disappeared. The ash content (% m/m) is then determined from the weight. The iron content from the ash sample is determined by using methods described in SABS 905 and BS 3773. The rest of the metal contents as well as the sodium content is determined with induction coupled plasma spectroscopy. A Varian Liberty 110 ICP was used. In this method, a plasma absorbs sufficient power from an external source to maintain the temperature at a level at which further ionisation sustains the plasma to flow indefinitely (Skoog and Leary, 1992). The external source of power for induction coupled plasma spectroscopy is a powerful radio frequency. (The plasma is an electrical conducting gaseous mixture that contains a significant concentration of cations and electrons, such that the net charge approaches zero. Argon ions and electrons are such conducting species.)

MOA No QCM

The sulphate content is determined by using an HP 8452 diode array spectrophotometer. The method is based on the method described by Jeffery *et al.* (1989) for measuring turbidity. Standard 0 mg/l, 10 mg/l, 20 mg/l and 50 mg/l sulphate solutions are made up. Five ml glacial acetic acid and 5 ml (10 m/v %) barium chloride is added to the standards and a standard curve drawn up on the spectrophotometer. A sample (± 0,2 to 1 g) is weighed accurately in a 100 ml volumetric flask and diluted to 60 ml with deionised water. Five ml glacial acetic acid and 5 ml 10 m/v % barium chloride is added. The absorbances are determined and compared with the calibration curve determined with the standard solutions.

APPENDIX C

Specification sheets of Dicalite 4151

Chemserve Perlite
Member of the Chemical Services Group

DICALITE 4151

Dicalite 4151 is a perlite filter aid, which is food grade approved and non-toxic. It can be used to filter edible oils, sulphur, chrome solutions and industrial chemicals.

1. **PERMEABILITY** : 1,46 - 2,28 Darcies (water at 30°C)

2. **RELATIVE FLOWRATE**[(a)] : 102 - 133

3. **FLOATS** : Max 10% (v/v)

4. **WET CAKE DENSITY** : 175 - 220 kg/m^3

5. **TYPICAL SIEVE ANALYSIS**[(b)]

Sieve Aperture (microns)		Mass (%)
on	106	13
on	45	47
on	25	74
pass	25	26

6. PACKAGING

16kg in paper bags.

(a) Water permeability flow ratio (PFRv).
(b) Wet screen method. Screen analysis is not a quality control test.

Chemserve Perlite
Member of the Chemical Services Group

TYPICAL PHYSICAL & CHEMICAL PROPERTIES OF PERLITE

1. Typical Physical Characteristics

Colour	white
Refractive index	1,5
Maximum free moisture	0,5%
Specific gravity	2,2 - 2,4
Softening point	870 – 1 093°C
Fusion point	1 260 – 1 343°C
Specific heat	837 J/kg.K

2. Typical Chemical Analysis

		Weight %
Silicone oxide	(SiO_2)	76,2
Aluminium oxide	(Al_2O_3)	12,1
Potassium oxide	(K_2O)	4,9
Sodium oxide	(Na_2O)	3,4
Iron oxide	(Fe_2O_3)	0,7
Calcium oxide	(CaO)	0,6
Magnesium oxide	(MgO)	0,1
Manganese oxide	(MnO)	0,1
Titanium oxide	(TiO_2)	0,1
Loss on ignition		1,9

EXPLANATIONS OF SOME TECHNICAL TERMS

1. Permeability

Permeability is the fundamental characteristic, which differentiates one filter aid grade from another when the particles are formed into a filter cake. Permeability is related to particle size distribution and can be expressed in various ways, e.g. as a relative flowrate or Darcies.

2. Darcy

A material having a permeability of 1 Darcy unit passes 1 ml per second per cm^2 of a liquid of I centipoise viscosity through a cake of 1 cm thickness at a pressure differential of 1 atmosphere.

3. Relative Flowrate (PFRv)

The relative flowrate is a ratio of the cake thickness and time taken for a constant volume of water to pass through a constant mass of filter aid.

4. Floats

In the milling and classifying of expanded perlite a small amount of glass bubbles stay intact. These particles tend to float on the surface of a liquid. The outside areas of these particles have precisely the same structure as other perlite particles and will therefore act the same during filtration or pre-coating.

Chemserve Perlite
Member of the Chemical Services Group

WHAT IS PERLITE?

Perlite is not a trade name but a generic term for naturally occurring siliceous volcanic rock. The distinguishing feature which sets Perlite apart from other volcanic glasses is that when heated to a suitable point in its softening range it expands twenty times its original volume or more.

This expansion is due to the presence of 2% to 6% combined water in the crude Perlite rock. The water became entrapped into the amorphous material on instant cooling after an eruption. When quickly heated above 870°C the crude rock pops in a manner similar to popcorn. As the combined water vaporises, it creates countless tiny bubbles in the heat softened glassy particles. It is these tiny glass-sealed bubbles which account for the amazing lightweight and other exceptional physical properties of expanded Perlite.

The expansion process also creates one of Perlite's most distinguishing characteristics - its white colour. While the crude rock may range from transparent light grey to glossy black, the colour of expanded Perlite ranges from snowy white to greyish white.

Dicalite Perlite Filter Aids are manufactured by crushing and classifying the ore particles into different grades. These ore particles are then heat expanded. The expanded particles are then milled and classed into different filter aid grades.

APPENDIX D

Composition of phthalic anhydride residue used in laboratory scale experiments

Table D.1 Composition of phthalic anhydride residue used in laboratory experiments.

Analyses	m/m %
Total acidity as phthalic acid (by titration)	75,5
Free acidity as phthalic acid by non-aqueous titration	3,2
Phthalimide	2,2
Benzoic acid	450 ppm
Anthraquinone	735 ppm
Naphthaquinone	< 100 ppm
SO_4	< 20 ppm
Ash sample analyses	
Cu	328 ppm
Fe	15,3
Cr	2,7
Mn	0,23
Ni	2,4
Ca	0,28
Mg	0,11
Na	774 ppm
Al	309 ppm
Ti	39 ppm
V	184 ppm
Mo	0,12

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APPENDIX E

Analysis of phthalic anhydride residue after distillation

LABORATORY REPORT NO	:	AS2000.387
SAMPLE IDENTIFICATION	:	PA Residue sample after PA has been distilled out of the PA residue.
ANALYSIS REQUESTED	:	As in table.
SUBMITTED BY	:	Karen van Staden and Magrieta Snyman.
ANALYST	:	Les Cornish, Danny Nilson, Marius MacDonald.
DATE	:	26/06/2000

Analyses	
Ash	21,8 %
The following analyses were done on the ash sample and calculated on the ash figures:	
Cu	18 ppm
Fe	2,0 %
Cr	16 ppm
Mn	53 ppm
Ni	25 ppm
Ca	100 ppm
Mg	22 ppm
Na	35,7 %
Al	58 ppm
Ti	9,6 ppm
V	54 ppm
Mo	12 ppm

Comments :

There appears to be no PA present in the sample.
The ash sample fizzed when HCl was added to dissolve the sample for the ICP analyses indicating the presence of carbonate.
It is assumed that the balance of the ash is carbon due to the colour of the residue.

APPENDIX F

Variables of laboratory experiments

Table F.1 Results of Experiment A.

Variable \ Experiment		A1	A2	A3
Mass phthalic anhydride residue (g)		30,030	30,081	30,032
Mass Dicalite 4151 (g)		9,000	9,048	9,001
Time (minutes)	Phthalic anhydride residue transferred to flask	11:25	8:15	9:08
	Flask immersed in hot oil bath	11:25	8:15	9:08
	Phthalic anhydride residue melted	12:30	9:20	10:15
	Dicalite transferred	12:30	9:20	10:15
	Agitator on	12:30	9:20	10:15
	Vacuum applied	12:40	9:30	10:23
	Vacuum released	14:10	11:20	14:00
	Flask removed from hot oil bath	14:10	11:20	14:00
	Agitator switched off	14:25	11:35	14:15

Table F.2 Results of Experiment B.

Variable \ Experiment		B1	B2	B3
Mass phthalic anhydride residue (g)		30,014	30,096	30,082
Mass Dicalite 4151 (g)		6,010	5,994	6,050
Time (minutes)	Phthalic anhydride residue transferred to flask	9:20	12:05	8:45
	Flask immersed in hot oil bath	9:20	12:05	8:45
	Phthalic anhydride residue melted	10:00	13:05	9:35
	Dicalite transferred	10:00	13:05	9:35
	Agitator on	10:00	13:05	9:35
	Vacuum applied	10:15	13:15	9:45
	Vacuum released	10:45	13:55	11:00
	Flask removed from hot oil bath	11:00	13:55	11:00
	Agitator switched off	14:20	14:10	11:15

Table F.3 Results of Experiment C.

Variable / Experiment		C1
Mass phthalic anhydride residue (g)		30,025
Mass Dicalite 4151 (g)		3,045
Time (minutes)	Phthalic anhydride residue transferred to flask	8:39
	Flask immersed in hot oil bath	8:39
	Phthalic anhydride residue melted	9:40
	Dicalite transferred	9:40
	Agitator on	9:40
	Vacuum applied	9:50
	Vacuum released	11:40
	Flask removed from hot oil bath	11:40
	Agitator switched off	11:55

Table F.4 Results of Experiment D.

Variable / Experiment		D1	D2	D3
Mass phthalic anhydride residue (g)		30,094	30,052	30,043
Mass Dicalite 4151 (g)		4,509	4,510	4,507
Time (minutes)	Phthalic anhydride residue transferred to flask	12:20	8:15	11:00
	Flask immersed in hot oil bath	12:20	8:15	11:00
	Phthalic anhydride residue melted	13:15	9:15	12:00
	Dicalite transferred	13:15	9:15	12:00
	Agitator on	13:15	9:15	12:00
	Vacuum applied	13:25	9:25	12:10
	Vacuum released	14:25	10:30	14:10
	Flask removed from hot oil bath	14:25	10:30	14:10
	Agitator switched off	14:35	10:40	14:20

APPENDIX G

Process variables of plant trials

Table G.1 Results of Experiment E.

Variable \ Experiment		E
Mass phthalic anhydride residue (kg)		699
Mass Dicalite 4151 (kg)		252
Time (hours)	Dicalite 4151 loaded	17/10/01 14:00
	Oil flow on	17/10/01 14:00
	Phthalic anhydride residue transferred	18/10/01 11:00
	Transfer complete	18/10/01 11:10
	Agitator on	18/10/01 11:00
	Vacuum applied	18/10/01 15:00
	Vacuum released	18/10/01 16:00
	Oil flow off	19/10/01 07:30
	Agitator off	19/10/01 10:00

Table G.2 Results of Experiment F.

Variable \ Experiment		F
Mass phthalic anhydride residue (kg)		1 562
Mass Dicalite 4151 (kg)		300
Time (hours)	Dicalite 4151 loaded	22/10/01 10:00
	Oil flow on	22/10/01 11:00
	Phthalic anhydride residue transferred	24/10/01 15:45
	Transfer complete	24/10/01 16:00
	Agitator on	24/10/01 15:45
	Vacuum applied	24/10/01 16:35
	Vacuum released	25/10/01 02:30
	Oil flow off	25/10/01 07:00
	Agitator off	27/10/01 11:00

Table G.3 Volume of phthalic anhydride collected – Experiment F.

Time of level measurement	Residue distillation collection tank volume (litres)
24/10/01 15:45	314
24/10/01 18:45	490
24/10/01 20:25	750
24/10/01 21:30	880
2410/01 22:30	946
24/10/01 23:30	978
25/10/01 00:10	1 076
25/10/01 02:30	1 244

Table G.4 Rate of distillation for Experiment F.

Time (minutes)	Time difference (minutes)	Mass phthalic anhydride in tank (kg) *	Mass phthalic anhydride in tank - difference (kg)	Rate of distillation (kg/minute)
0	-	374,916	-	-
115	115	585,060	210,144	1,823
215	100	895,500	310,440	3,104
380	65	1050,72	155,220	2,388
605	60	1 129,524	78,804	1,313
890	60	1 167,732	38,2080	0,637
1 215	40	1 284,744	117,012	2,925
1 680	140	1 485,336	200,592	1,433

* Mass phthalic anhydride distilled off = litres (Table G.3) × 1,194 kg/λ (density of phthalic anhydride at 153°C).

Table G.5 Results of Experiment G.

Variable \ Experiment		G
Mass phthalic anhydride residue (kg)		947
Mass Dicalite 4151 (kg)		260
Time (hours)	Dicalite 4151 loaded	29/10/01 13:00
	Oil flow on	29/10/01 12:30
	Phthalic anhydride residue transferred	30/10/01 18:27
	Transfer complete	30/10/01 19:15
	Agitator on	30/10/01 18:20
	Vacuum applied	30/10/01 21:10
	Vacuum released	See Table G.6.
	Oil flow off	Remained on.
	Agitator off	31/10/01 16:30

Table G.6 Vacuum application and volume of phthalic anhydride collected – Experiment G.

Vacuum on	Vacuum off	Residue distillation collection tank volume before vacuum (litres)	Residue distillation collection tank volume after vacuum (litres)
30/10/01 21:10	30/10/01 22:30	1 244	1 244
31/10/01 11:13	31/10/01 16:00	1 244	1 244

Table G.7 Results of Experiment H.

Variable / Experiment		H
Mass phthalic anhydride residue (kg)		1 259
Mass Dicalite 4151 (kg)		380
Time (hours)	Dicalite 4151 loaded	02/11/01 13:00
	Oil flow on	01/11/01 12:00
	Phthalic anhydride residue transferred	06/11/01 10:55
	Transfer complete	06/11/01 11:05
	Agitator on	06/11/01 10:45
	Vacuum applied	06/11/01 11:40
	Vacuum released	See Table G.8.
	Oil flow off	08/11/01 08:30
	Agitator off	08/11/01 16:00

Table G.8 Vacuum application and volume of phthalic anhydride collected – Experiment H.

Vacuum on	Vacuum off	Residue distillation collection tank volume before vacuum (litres)	Residue distillation collection tank volume after vacuum (litres)
06/11/01 11:40	06/11/01 12:34	1 244	1 316
06/11/01 15:10	06/11/01 17:45	1 316	1 350
06/11/01 20:40	06/11/01 22:45	1 350	1 388
06/11/01 24:45	07/11/01 01:10	1 388	1 388
07/11/01 03:00	07/11/01 04:25	1 388	1 458
07/11/01 07:45	07/11/01 09:45	1 458	No measurement taken.
07/11/01 11:25	07/11/01 12:42	No measurement taken.	No measurement taken.
07/11/01 13:30	07/11/01 14:55	No measurement taken.	No measurement taken.
07/11/01 17:35	07/11/01 19:50	No measurement taken.	1 494
07/11/01 22:50	08/11/01 02:00	1 494	1 530
08/11/01 05:00	08/11/01 11:50	1 530	1 564

Table G.9 Rate of distillation for Experiment H.

Time (minutes)	Time difference (minutes)	Mass phthalic anhydride in tank (kg) *	Mass phthalic anhydride in tank - difference (kg)	Rate of distillation (kg/minute)
0	-	1 485,336	-	-
350	350	1 571,304	85,968	0,246
435	85	1 657,272	85,968	1,011
495	60	1 657,272	0	0
605	110	1 740,852	83,58	0,760
707	102	1 783,836	42,984	0,421
1 092	385	1 826,82	42,984	0,112

* Mass phthalic anhydride distilled off = litres (Table G.8) × 1,194 kg/λ (density of phthalic anhydride at 153°C).

Table G.10 Results of Experiment I.

Variable / Experiment		I
Mass phthalic anhydride residue (kg)		1 326,04
Mass Dicalite 4151 (kg)		160
Time (hours)	Dicalite 4151 loaded	10/11/01 10:30
	Oil flow on	08/11/01 16:30
	Phthalic anhydride residue transferred	08/11/01 21:30
	Transfer complete	08/11/01 21:45
	Agitator on	08/11/01 21:45
	Vacuum applied	08/11/01 21:45
	Vacuum released	See Table G.11.
	Oil flow off	10/11/01 22:00
	Agitator off	12/11/01 09:30

Table G.11 Vacuum application and volume of phthalic anhydride collected – Experiment I.

Vacuum on	Vacuum off	Residue distillation collection tank volume before vacuum (litres)	Residue distillation collection tank volume after vacuum (litres)
09/11/01 21:45	09/11/01 22:30	1 564	1 602
10/11/01 01:00	10/11/01 04:30	1 602	1 674
10/11/01 07:05	10/11/01 08:50	1 674	1 712
10/11/01 10:55	10/11/01 12:50	1 712	1 750
10/11/01 16:25	10/11/01 18:30	1 750	1 788
10/11/01 21:46	11/11/01 00:50	1 788	1 856
11/11/01 02:15	11/11/01 04:30	1 856	1 900
11/11/01 04:50	11/11/01 10:00	1 900	No measurement taken.
11/11/01 12:50	11/11/01 17:30	No measurement taken.	2 128

Table G.12 Rate of distillation for Experiment I.

Time (minutes)	Time difference (minutes)	Mass phthalic anhydride in tank (kg) *	Mass phthalic anhydride in tank - difference (kg)	Rate of distillation (kg/minute)
0	-	1 867,416	-	-
45	45	1 912,788	45,372	1,008
155	150	1 998,756	85,968	0,573
180	25	2 044,128	45,372	1,815
310	130	2 089,540	45,372	0,349
435	125	2 134,872	45,332	0,363
619	184	2 216,064	81,192	0,441
754	135	2 268,600	52,536	0,389
1 034	280	2 540,832	272,232	0,972

* Mass phthalic anhydride distilled off = litres (Table G.11) × 1,194 kg/λ (density of phthalic anhydride at 153°C).

APPENDIX H

Analysis of samples collected in plant scale experiments

Table H.1 Composition of samples collected in Experiment F.

Sample / Compound	SP1	SP3	SP4	SP5
Phthalic anhydride (% m/m)	99,02	74,9	55,5	96,3
Phthalimide (% m/m)	0,15	0,69	0,61	0,99
Benzoic acid (% m/m)	0	0,63	1,23	0,63
Anthraquinone (ppm)	-	640	610	208
Naphthaquinone (ppm)	2 903	< 100	< 100	< 100
SO_4 (ppm)	-	< 10	< 10	< 10
Ash (% m/m)	-	3,28	20,23	0,18
Ash sample analyses				
Fe (% m/m)	-	9,28	1,93	9,93
Cr (ppm)	-	2,9	< 0,5	2 300
Mn (ppm)	-	281	54	67
Ni (ppm)	-	16	< 0,5	935
Cu (ppm)	-	122	65	1 665

SPx refer to the sampling points as indicated in Section 3.1.2, Figure 3.1.

SP2 samples were not collected due to operational problems experienced with production capacity.

Table H.2 Composition of samples collected in Experiment G.

Sample / Compound	SP1	SP3	SP4	SP5
Phthalic anhydride (% m/m)	99,48	52,7	19,8	96,2
Phthalimide (% m/m)	0,13	1,59	0,54	1,04
Benzoic acid (% m/m)	0	0,21	0,59	0,63
Anthraquinone (ppm)	-	1 295	691	282
Naphthaquinone (ppm)	2 803	< 100	< 100	< 100
SO_4 (ppm)	-	< 10	< 10	< 10
Ash (% m/m)	-	4,64	51,75	0,06
Ash sample analyses				
Fe (% m/m)	-	5,7	8 265 ppm	5,69
Cr (ppm)	-	< 0,5	264	11
Mn (ppm)	-	127	52	127
Ni (ppm)	-	170	162	20
Cu (ppm)	-	179	50	94

SPx refer to the sampling points as indicated in Section 3.1.2, Figure 3.1.

SP2 samples were not collected due to operational problems experienced with production capacity.

Table H.3 Composition of samples collected in Experiment H.

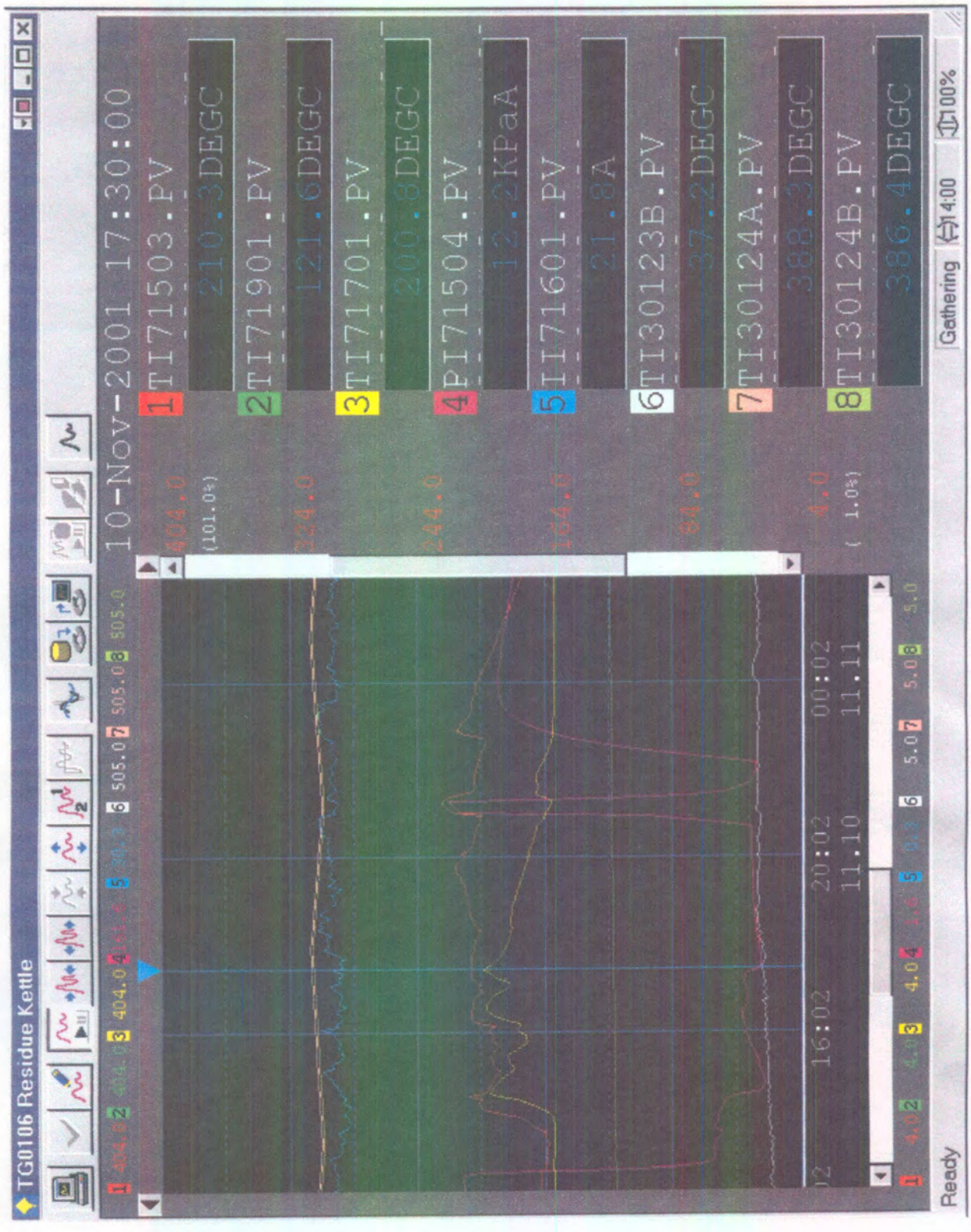
Sample / Compound	SP1	SP3	SP4	SP5
Phthalic anhydride (% m/m)	99,40	60,2	1,95	96,2
Phthalimide (% m/m)	0,16	1,84	298	1,04
Benzoic acid (% m/m)	0	0,19	0,63	0,63
Anthraquinone (ppm)	-	684	143	282
Naphthaquinone (ppm)	1 298	< 100	< 100	< 100
SO_4 (ppm)	-	< 10	< 10	< 10
Ash (% m/m)	-	9,71	47,04	0,06
Ash sample analyses				
Fe (% m/m)	-	2,77	2,88	43,23
Cr (ppm)	-	< 0,5	< 0,5	5 809
Mn (ppm)	-	74	99	437
Ni (ppm)	-	201	201	146
Cu (ppm)	-	80	62	1 016

SPx refer to the sampling points as indicated in Section 3.1.2, Figure 3.1.

SP2 samples were not collected due to operational problems experienced with production capacity.

APPENDIX I

Actual printout of plant's control parameters during Experiment I


TG0106 Residue Kettle
10-Nov-2001 17:30:00
1 TI71503.PV 210.3DEGC
2 TI71901.PV 121.6DEGC
3 TI71701.PV 200.8DEGC
4 PI71504.PV 12.2KPaA
5 II71601.PV 21.8A
6 TI30123B.PV 37.2DEGC
7 TI30124A.PV 388.3DEGC
8 TI30124B.PV 386.4DEGC
404.0
324.0
244.0
164.0
84.0
4.0
16:02
20:02
00:02
11.10
11.11
Gathering
4:00
100%
Ready