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Oxidation of Waxes Using Microwave-Generated Singlet Molecular Oxygen

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by

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ABSTRACT

Oxidation of Waxes Using Microwave-generated Singlet Molecular Oxygen

Waxes are a widely used chemical commodity throughout the world due to certain intrinsic properties. Applications vary widely, including such obvious ones as candles and polishes, less obviously coatings, ink, and cosmetics, and more obscurely, hot melt adhesives, textile processing and chewing gum. The waxes used are obtained from a variety of sources, natural, mineral, and synthetic.

The properties of the wax determine its suitability for a particular application. For certain of the latter, a wax containing oxygen groups is often the most appropriate type. While there are a number of such waxes that occur naturally, there are also many more in which the raw wax has undergone oxidation by chemical processes. Generally this is done utilising elevated temperatures, and passing air or oxygen through the wax. Oxidation then takes place via a free radical process.

Singlet molecular oxygen is a higher-energy state species of oxygen, in which the two electrons in the π^* 2p antibonding molecular orbitals, while remaining unpaired, are excited to antiparallel spin. Reactions of singlet oxygen are very site-specific, resulting in more specific products compared to the free radical process. It was considered that oxidation of waxes by reaction with singlet oxygen might produce different products compared to the thermal oxidation, and also compared to oxidation using ozone.

An apparatus was set up to test this theory. The singlet oxygen was generated by passing a stream of oxygen through a microwave beam to form a plasma, the resulting singlet oxygen-containing gas being reacted with molten wax. Optimisation of the setup was performed before performing reactions, using several different waxes. The experiments were duplicated by ones with the microwave switched off, so that any results could be ascribed to the presence of singlet oxygen, and not normal oxygen.

A similar apparatus was set up to react the same waxes with ozone, the latter being generated by passing oxygen through an electrical discharge-type generator. Blank runs with the electric discharge apparatus switched off, were also carried out to be able to distinguish any reaction due to the unozonised oxygen.

The results showed that the singlet oxygen only reacted with a particular type of wax, namely oxidised polyethylene wax (AC629), although other effects were caused by the heat of the plasma. The ozone, on the other hand, reacted readily with all types of waxes tested.

Other experiments were also conducted to investigate the use of microwave technology for chemical purposes, including development of an analytical method for saponification value determination in which microwaves replaced conventional heating.

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CHAPTER 1: INTRODUCTION

Around the world, over 30 000 metric tonnes (mt) of waxes are oxidised each year [1].This supplements the *ca.* 30 000 mtpa of natural waxes such as carnauba, montan, beeswax and others which contain oxygen functional groups [2].The feedstock for oxidation is almost entirely the *synthetic* waxes, which are of two types: the polyethylene waxes, polymerised from ethylene, and the Fischer-Tropsch waxes, sometimes called polymethylene waxes, which are manufactured from synthesis gas. The latter may be derived from coal, or from natural gas.

Oxidised waxes have a myriad of uses, ranging from humble polishes to advanced technology water-based inks [3,4]. Initially, they were a means of replacing scarce and/or expensive natural waxes, which are now mostly used for food related applications, although even here, the synthetic waxes have made some inroads, albeit in unoxidised form [5].

Commercial scale oxidations have been in operation since the nineteen-fifties [6]. While each company's process technology is proprietary information, it is known that practically all involve reacting air with the liquid wax. The purpose of this research project was to investigate two alternative and novel methods of oxidation as applied to waxes, namely oxidation using excited-state singlet oxygen generated by microwaves, and ozonolysis, a standard method in organic chemistry.

This chapter intends to give the reader some background knowledge of the different types of waxes, the current means of wax oxidation , the microwave-induced generation of singlet oxygen, and ozonolysis.

1.1 Waxes

Different sources tend to define waxes differently, but it is generally agreed that they are hydrocarbon-based materials, and solid at room temperature. However, even this definition is not all-embracing, as there now exist *silicone* waxes, and there are a few waxes which are semi-liquid at room temperature (25°C). While a glossary of terms used by wax chemists is included in Chapter 6, it is necessary to explain a few of them at this point as they will be frequently used henceforth.

Acid value or *number* refers to the concentration of carboxylic acid groups contained in the wax.

Saponification value refers to the concentration of acids *plus* esters in the wax.

Congealing point is one of the (many) ways of describing the melting point of a wax.

Penetration is a measure of wax hardness. The temperature at which the measurement was made is always quoted.

The glossary should be referred to for further details.

Waxes are usually classified according to their source. These are: *natural* (animal, vegetable, and mineral), *petroleum*, and *synthetic*.

The *natural* waxes all contain oxygenates and chemistry texts often group them with fats and oils due to their similar chemical compositions. Animal waxes cover a wide variety of products, but tend to have quite similar chemical compositions, comprising long chain fatty acids of length C_{20}-C_{30}. They also contain ester groups and hydroxyl groups. The most important of these waxes from the commercial point of view are *beeswax* and *lanolin*, the latter being derived from sheep's wool. Both are soft waxes, and are often subject to chemical bleaching to improve their colour.

Beeswax has been commercially used for thousands of years. Production nowadays is *ca.* 8 000 mtpa, being mainly used in polishes and cosmetics [7]. It has been studied fairly extensively in the past and compared to most other waxes, its chemical composition is quite well defined. See Table 1.

Table 1 : Composition of beeswax [8]

Acid value	~ 20 mgKOH/g
Saponification value	~ 84 mgKOH/g
Penetration @ 25°C	~ 20 mm x 10^{-1}*
Congealing point	~ 64°C

*Units of penetration are *tenths* of a millimeter, abbreviated as shown.

Availability of more abundant and cheaper sources has led to replacement of beeswax in many applications by petroleum waxes and oxidised synthetic waxes, the latter most closely resembling the beeswax chemically.

Lanolin is recovered from wool and is a very soft, almost grease-like wax. Its chemical composition is similar to beeswax with respect to ester and acid contents, but chain lengths are smaller, being in the range C_8-C_{28}. Lanolin is used in cosmetic and pharmaceutical applications, where its softness is an advantage.

A huge number of plants, especially in more arid regions, secrete wax in order to protect themselves from dehydration. Commercially, the most important are *carnauba*, (~10000 mtpa) and, in smaller quantities, *candelilla* wax (~ 2 000 mtpa). These vegetable waxes are much harder than the animal waxes mentioned above. Carnauba wax is higher in ester content than both the animal waxes and the candelilla, while the latter is much higher in hydrocarbon (i.e. non-functionalised) content. The approximate compositions of these waxes are shown in table 2.

Table 2 : Composition of carnauba and candelilla waxes [8]

	Carnauba	Candelilla
Acid value (mgKOH/g)	~ 8	~ 15
Saponification value (mgKOH/g)	~ 80	~ 55
Penetration @ 25°C (mm x 10^{-1})	~0.5	~1.0
Congealing point (°C)	~68	~69

There are a number of mineral waxes, sometimes termed *fossil* waxes, but only *montan* wax is of commercial importance. Montan wax is recovered by solvent extraction of lignite (brown coal). The solvent which has been in use is a benzene-alcohol mixture, but after extraction further refining is required (bleaching most commonly), before the wax can be used. Various grades are available, with a large proportion being further chemically modified to produce *ester* waxes, e.g. by Hoechst in Germany. Raw montan wax is a very hard, almost black wax whose colour is improved to pale yellow by bleaching, although this operation also leads to some softening of the wax. Montan wax is largely produced in (the former East) Germany, but environmental considerations are eroding the economics of these operations.

Production of montan wax is currently ~20 000 mtpa with the main use being in polishes, and in chemically modified form as paper coatings, emulsion polishes, and lubricants for plastics processing. Table 3 compares the properties of some montan waxes of different grades.

Table 3 : Properties of montan waxes [9]

WAX	Crude	Bleached	Esterified *	Esterified/ saponified **
Acid value (mgKOH/g)	30	120	18	12
Saponification value (mgKOH/g)	65	150	150	110
Congealing point (°C)	82	82	80	105

*Hoechst-Wachs E

** Hoechst-Wachs OP

The *petroleum* waxes, as their name implies, are recovered from crude oil during the refining process. The waxes are recovered by deoiling, normally by 'sweating', although solvent extraction is also used but is slowly being replaced for economic and enviromental reasons. Crude oils vary in wax content, with some being practically wax-free, e.g. from Tampico in Mexico, while others, e.g. from Assam in Myanmar, may contain as much as 10%. The petroleum waxes are distinguished from the natural waxes by their complete lack of functional group content, being totally hydrocarbon in composition. The waxes are separated into two categories, *paraffin* and *microcrystalline*, with the former being further classified according to their residual oil content into *fully refined* or *semi-refined*. The paraffin waxes are mostly of normal paraffin with some iso paraffin content, while the microcrystalline waxes have a large proportion of iso and cyclic content.

Both types of wax are extensively used for coatings (paper and cardboard), while a large proportion of paraffin waxes are still consumed for the manufacture of candles [10]. The microcrystalline waxes are also used in hot-melt adhesives, electrical coatings, and chewing gum [11]. Table 4 shows the typical properties of the three main types of paraffin waxes.

Table 4 : Properties of petroleum waxes

	Semi-refined	Fully refined	Microcrystalline
Congealing pt. (°C)	58	61	83
Penetration @ 25°C (mm x 10^{-1})	20	11	13
MEK solubles (mass %)	1.5	0.2	3

The *synthetic* waxes fall into two categories: polyolefin (mainly polyethylene, with a few polypropylene types), and Fischer-Tropsch waxes. Both types have only come into widespread use since the nineteen-fifties. Both types to some extent were also originally seen as by-products, of plastic manufacture in the case of polyolefins and liquid fuel production in the case of Fischer-Tropsch (FT) waxes.

The polyolefin waxes are manufactured by polymerisation of ethylene (or propylene) to molecular weights of < 3000 g mol^{-1},although a few are as high as 4000 g mol^{-1}. Many of the polyolefin waxes are unfunctionalised but there are some co-polymerised types in which a functionalised monomer has been added to the hydrocarbon monomer. Some are also modified by post-polymerisation processes, such as oxidation.

The FT waxes are formed from synthesis gas ($CO + H_2$) and can be described as polymers of methylene. Waxes produced by the FT process are distinguished by their extremely low content of branched (iso) chains, resulting in low viscosities when in the liquid phase compared to the polyethylene waxes. Molecular weights of the FT waxes are generally lower than the polyolefin waxes, being closer to the natural waxes (< 1000 g mol^{-1}). FT waxes are functionalised by post-synthesis processes.

Table 5 shows some typical properties of various synthetic waxes.

Table 5 : Properties of synthetic waxes

Wax	H2	A28	AC6	AC629	N15
Acid value (mgKOH/g)	0	28	0	15	0
Sap. value* (mgKOH/g)	0	56	0	32	0
Penetration @ 25°C (mm x 10^{-1})	<1	3	3	5	0.6
Congealing pt. (°C)	96	90	94	92	163

*Sap. value is the normal abbreviation for saponification value

H2 = Paraflint H2, an FT wax [12]

A28 = Paraflint A28, an oxidised FT wax

AC6 = Allied Chemicals AC6, a polyethylene wax [13]

AC629 = Allied Chemicals AC629, an oxidised polyethylene wax

N15 = Epolene N15, a polypropylene wax [14]

The synthetic waxes are found in a large number of applications. They have taken over some of the markets formerly held by natural waxes, particularly in oxidised form, where they have become more economically attractive. They have also been used in new applications as a result of their availability and specific properties. Inks, hot melt adhesives, liquid polishes and textile processing are large consumers of synthetic waxes.

1.2 Oxidation of Waxes

Oxidation is the most common technique used to modify waxes, particularly the synthetic waxes. Very few of the other types of wax are in fact used in modified form, apart from the montan waxes. As mentioned previously, the montan waxes are subject to a number of chemical treatments (including oxidation by treatment with chromic and sulfuric acids).

But why oxidise the wax in the first place? The brief overview given above showed that all of the natural waxes have oxygen containing groups as part of their structure. This endows them with certain properties which can be advantageous in certain applications. These properties are the result of the introduction of some polarity to the wax and this makes them more compatible with many organic solvents (important for paste polishes used for shoes, floors, etc.) and also adds hydrophilic characteristics. This is especially important as this assists in emulsification of the wax. Wax emulsions are useful for liquid polishes, inks and as textile processing aids. Present day environmental considerations are also forcing a move to water-based materials, away from solvent based systems.

Wax oxidations have been commercial processes since just after the introduction of synthetic waxes. The essential feature of each manufacturer's process has been the reaction of air or oxygen with the liquid wax at temperatures above 130° C and often higher. Most of the initial development work was done on liquid paraffins to obtain fatty acids, later including the softer petroleum waxes. This work was done in Germany during World War II to replace natural fatty acids, which could no longer be obtained due to the British blockade. While some of these fatty acids were esterified to produce edible fats, e.g. for margarine, the major use was for soaps, a practice which continued after the war. The processes normally employed a catalyst such as potassium permanganate and were carried out at temperatures below 140°C, the oxidation taking up to thirty hours to complete [15].

This form of oxidation, known as Liquid Phase Oxidation (LPO) [16], has since been widely adopted for the oxidation of lighter hydrocarbons, such as butane, in the manufacture of products like acetic acid and methyl ethyl ketone. In fact, in economic terms oxidation of these light paraffins and aromatics is much more important than wax oxidation. Over a million tons of light hydrocarbons are oxidised each year compared to ~40 000 mtpa of synthetic wax.This figure is also much less than the ~400 000 mtpa of fatty acids being produced by oxidation of petroleum waxes [17].

These liquid phase oxidations take place via a free radical mechanism first described by Semenov [18] in 1935 and the generally accepted mechanism is shown below:

$$RH \rightarrow R\bullet + H\bullet$$

$$R\bullet + O_2 \rightarrow ROO\bullet$$

$$ROO\bullet + RH \rightarrow ROOH + R\bullet\text{, etc.}$$

$$ROO\bullet + ROO\bullet \rightarrow ROOR + O_2$$

$$ROOH \rightarrow RO\bullet + HO\bullet$$

$$RO\bullet + RH \rightarrow ROH + R\bullet$$

$$HO\bullet + RH \rightarrow H_2O + R\bullet$$

$$ROOH + RH \rightarrow 2ROH$$

$$ROOH \rightarrow R_1COR_2$$

$$R_1COR_2 + O_2 \rightarrow \text{acids}$$

Most of the mechanistic studies in the past have been carried out on the C1-C4 paraffins. There are two reasons for this: i) the oxidation of these compounds is important to the chemical industry due to the volume of products produced in this manner; and, ii) the identification of the oxidation products is relatively simple. More recent studies [20] have followed the oxidation of decane (C_{10}), but separation of the products is very complex, making both quantitative and qualitative analyses difficult. This has meant that most studies of wax oxidation have tended to be empirical in nature, the final properties of the wax being more important to the wax chemist than the exact synthetic route. This can be problematic when trying to decide what, or if, process control parameters can change any of the characteristics of the wax.

Liquid phase oxidation has therfore provided the basic technology for wax oxidation and in volume terms is most important. Fatty acid production by this method is now largely confined to Russia and a few of the other ex-Soviet bloc states where the cost of importing natural fatty acids does not make economic sense. This is reflected in the literature, where it can be seen that much of the work in the field has been carried out in Russia [15, 21-35].

1.3 Singlet Oxygen

Singlet oxygen is a higher-energy state species of molecular O_2. This state is achieved by the promotion of the two highest energy electrons occupying the π^*_{2p} molecular orbitals to antiparallel spins. In the ground state the two electrons have parallel spins and each occupies a separate π^*_{2p} orbital. In the singlet state ($^1\Delta_g$) the two electrons occupy one orbital but with antiparallel spins.It should be noted that another singlet species exists, namely the $^1\Sigma_g^+$ species

[36]. Here the electrons occupy the π^*_{2p} orbitals singly, but with antiparallel spin. However in the liquid phase the lifetime of the latter species is measurable only in nanoseconds, becoming a few minutes in the gas phase, so it is usually disregarded. The $^1\Delta_g$ state has a lifetime of around 45 minutes in the gas phase and a few milliseconds in the liquid phase [37]. Figure 1 shows the molecular orbital diagram for the three species. For clarity only the 2p orbitals are shown.

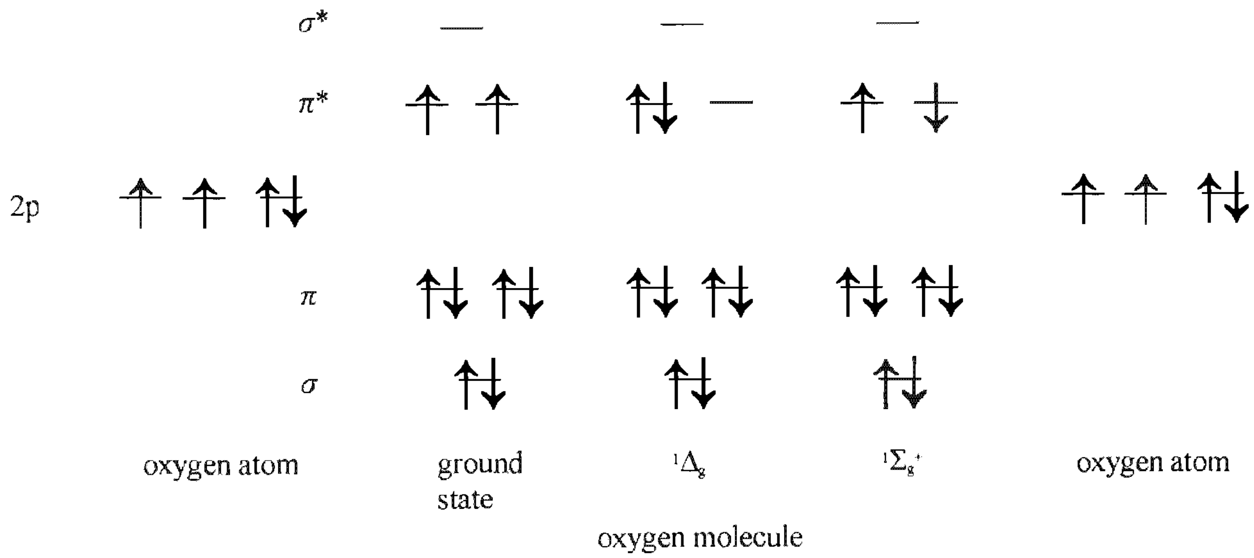


Figure 1: Molecular orbital diagrams showing the ground state and singlet $^1\Delta_g$ and $^1\Sigma_g^+$ states of O_2.

There are a variety of methods for generating singlet oxygen.The first method, discovered early in the twentieth century, is by photosensitisation [38-40]. A coloured sensitiser (dye) is subjected to visible or UV light in the presence of oxygen, bringing about the oxidation of the substrate.This method is being widely used in experimental chemistry despite some drawbacks [41-45], some of which, e.g. product separation, have been overcome by binding the sensitiser to a polymer [46-48]. Use of dyes for wax oxidation has been attempted in the Schümann Sasol Wax Research laboratories [49], but proved unsuccessful.

Chemical methods for generating singlet oxygen are also available [50-51] but have several disadvantages, the major one being that separation difficulties are increased. A more recent innovation has been the generation of gaseous singlet oxygen by microwave discharge [52-54]. While problems also exist with this route, it has the advantage of requiring no other chemicals, although non-singlet oxygen may have to be removed.

The reason for the interest in singlet oxygen is that it undergoes reactions at specific sites, generally leading to more specific products. The free radical process, as shown above, results in a complex mixture of oxygenated species with a variety of chain lengths because of the chain scission occurring during the process. Three mechanisms for reactions of singlet oxygen are recognised, which depend on the reactive substrate [37,55]. These three reaction types are discussed more fully in section 4.2. Thus far, only substrates with at least one double bond are known to be reactive with singlet oxygen.

In addition to its role in synthetic organic chemistry, singlet oxygen plays an important role in the photodegradation of polymers in air by autoxidation, and in reactions in the upper atmosphere [55].

1.4 Microwave-induced Plasmas

Gas plasmas produced by electromagnetic discharge have been actively utilised for almost thirty years. Most of the research carried out has been done in connection with spectroscopic analytical techniques [56]. Argon plasmas have found wide use as generators of steady-state concentrations of atoms and unstable molecules which can then be measured by e.g. atomic emission. This is the basis of the *Inductively Coupled Plasma* method of analysis [57-62]. However most of the plasmas have been generated at frequencies in the radio frequency (RF) range (27 - 56 MHz), while microwave plasmas are generated at 2.45 GHz in most instances. It has been reported that the lower temperatures of the microwave plasmas make sample introduction more difficult, although the microwave plasmas have been used at much lower powers, typically 100 W, compared to the RF plasmas which are normally run at 900-1200 W [63].

It was as the result of spectroscopic studies of microwave-induced plasmas that singlet oxygen species were positively identified, and it was realised that this provided a convenient source of gaseous singlet oxygen. Since then, microwave generation has been used as a major source for experiments with singlet oxygen [54].

Microwave spectroscopy is a well established technique for identifying molecules in the gas phase [64], also giving information on bond angles, bond lengths, and types of vibration. More recently, the use of microwaves as a novel method of heating has been extensively studied (see for instance, review by Strauss [65]).There is some debate as to whether microwaves may play a direct role in reactions [66], but it has been shown by many authors, e.g. Gedye [67], that microwave heating can shorten reaction times dramatically. Currently there is not much in the literature concerning the use of microwave-generated species, apart from singlet oxygen, as a source of reactants (but see Oumghar [68], where a microwave induced *air* plasma is being reacted with methane to form C_2 hydrocarbons).

1.5 Ozonation

Unlike singlet oxygen, ozone, the triatomic allotrope of oxygen, O_3, has been in use for about 150 years as an oxidising agent. It is chiefly utilised for water purification, both prior to consumption for potable use, and after, when it is used to detoxify waste water. Ozone is also being used as a bleaching agent, particularly in the paper industry for pulp treatment. A growing role is the application of ozone in synthetic organic chemistry, where it is readily added to unsaturated organic compounds, and is now being commercially utilised in the production of certain fragrances and other fine chemicals. Some medical treatments, e.g. elimination of cholesterol deposits, also involve the use of ozone [69].

Ozonolysis of hydrocarbons was reported as long ago as the early 1900's, but it is only since the nineteen-sixties that some effort has been made to find synthetically useful processes [70,71]. Much work on the oxidation of paraffins was done by Tyutyunnikov and co-workers in Russia but publications by the Russians in this field appear to have ceased by 1979 [72]. These papers are also the few which involve the use of ozone at temperatures above 25° C.

Ozone is generated by application of an electrical discharge of about 10 kV to either oxygen or air. Higher concentrations of ozone are obtainable from oxygen, but this is obviously more costly.

1.6 Objective of Research

The objective of this research was firstly, to investigate whether singlet oxygen would react with waxes, and secondly, to compare this with the use of ozone.

The use of microwave technology in this project was also of major importance, and experimental work was carried out to explore this aspect further. This included utilisation of microwaves to replace conventional heating, and the creation of plasmas using gases other than oxygen.

CHAPTER 2: EXPERIMENTAL APPARATUS AND DESIGN

The apparatus used essentially consisted of the following:- oxygen source; reactive species generator, and reaction vessel. The same reaction vessel was used for both singlet oxygen reactions and ozonolysis. Similarly, the oxygen source in both cases was from commercially available cylinders of 99. 999 % purity.

2.1 Singlet Oxygen Apparatus

A diagram and photographs of this apparatus is shown in Figures 2 and 3, respectively. The experimental design is similar to that described by Ogryzlo [54]. Oxygen from the cylinder was passed through a flowmeter, then through a control valve, which gave finer or more delicate control of the gas flow. This was required due to both the low flows and pressures which had to be maintained throughout an experiment. The gas then passed through a glass tube in which the plasma, and hence singlet oxygen, was generated. This tube passed vertically through an aluminium waveguide at an angle of 90° to the waveguide. Where the plasma tube went through the waveguide, the waveguide itself was extended by 15 cm (> one wavelength at 2.45 GHz) with a diameter of 6.1 cm (1/2 of a wavelength) to attenuate the microwaves and minimise leakage. A microwave detector was used to measure any leakage at the ports but measurements were below 1 $mWcm^{-2}$ at a distance of 5 cm. The waveguide was attached to a variable-power microwave generator [73], protected by a water-cooled circulator to prevent damage to the magnetron by reflected microwaves. This power of the reflected microwaves could be measured, enabling calculation of the power absorbed by the plasma.

The singlet oxygen thus generated was then bubbled via a small frit (gas distributor) into the molten wax. The flask holding the wax was placed on a hotplate to keep the wax in the liquid state. The flask, in turn, was connected to a vacuum pump via two cold traps, which then vented to atmosphere. The cold traps were filled with a solid carbon dioxide/ethanol slurry. A vacuum gauge was attached upstream of the cold traps.

An electric fan was used to keep the plasma tube, which was made from borosilicate glass, from overheating.

2.2 Ozonation Apparatus

A diagram and photographs of this apparatus are shown in Figures 4 and 5 respectively. Oxygen from a cylinder was fed into an electric discharge ozoniser [74]. The flow was set using a flowmeter built into the ozone generator, and the current adjusted to produce a specific concentration of ozone. The ozone-rich gas flowed into a glass tube, through a small frit (exactly the same as that used for the microwave experiments), and into the wax. The latter was once again contained in a flask standing on a hotplate to keep the wax molten. The flask vented into a scrubber holding buffered potassium iodide solution, which reduced the ozone to oxygen. This then vented into the atmosphere. The whole apparatus was placed under a fume extractor as a precaution against ozone leaks.

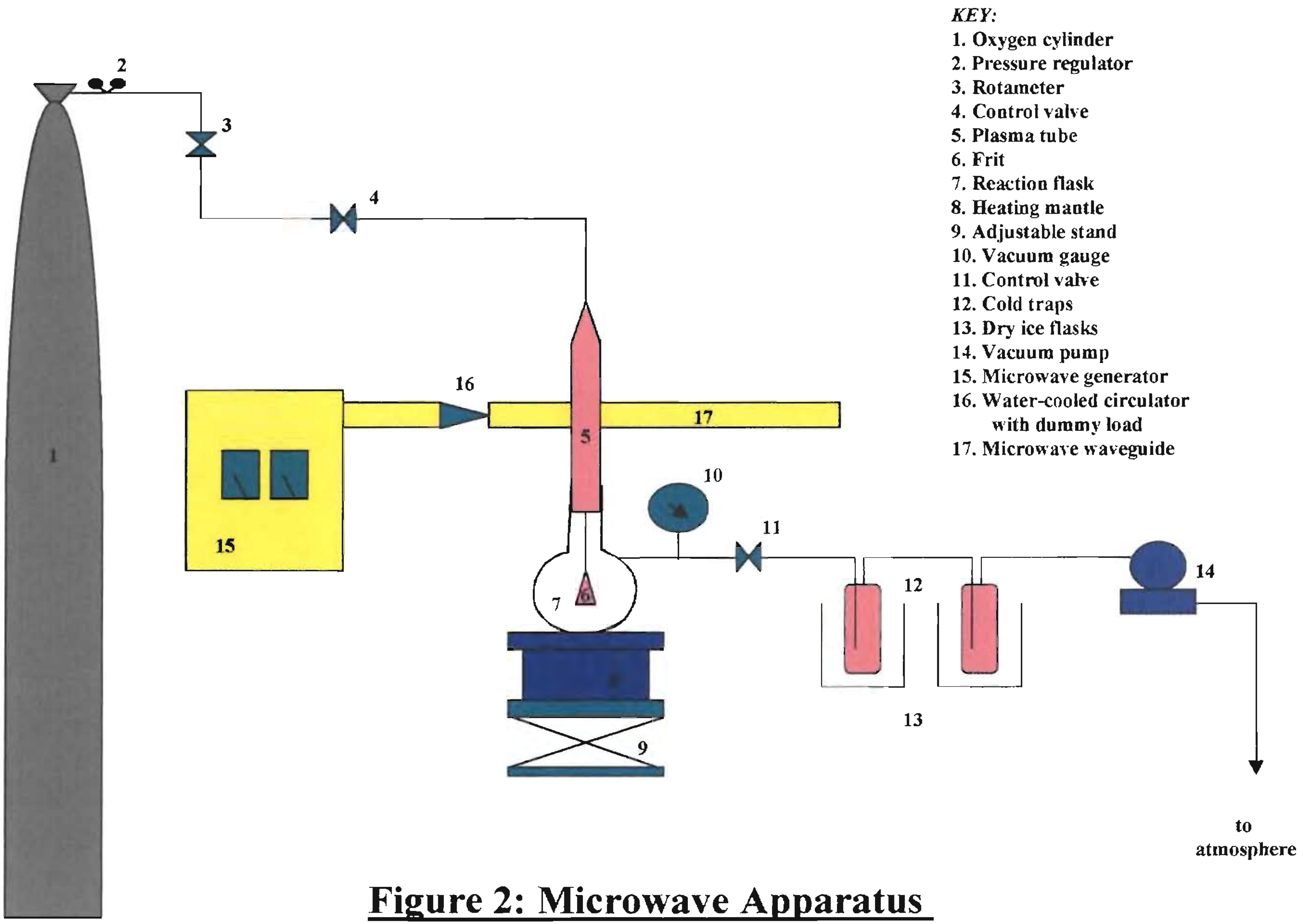


Figure 2: Microwave Apparatus

Figure 3: Photographs of the Microwave Apparatus

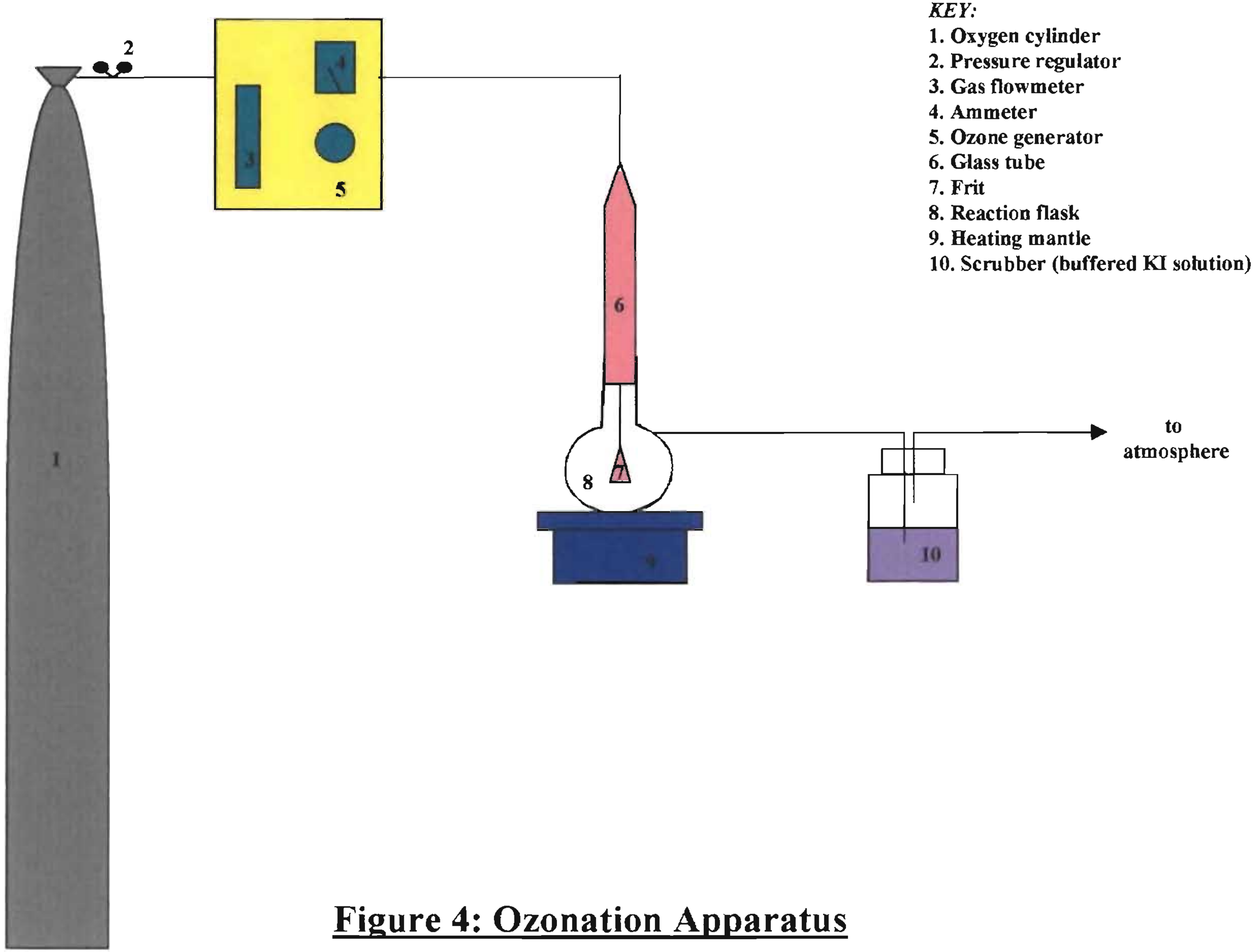


Figure 4: Ozonation Apparatus

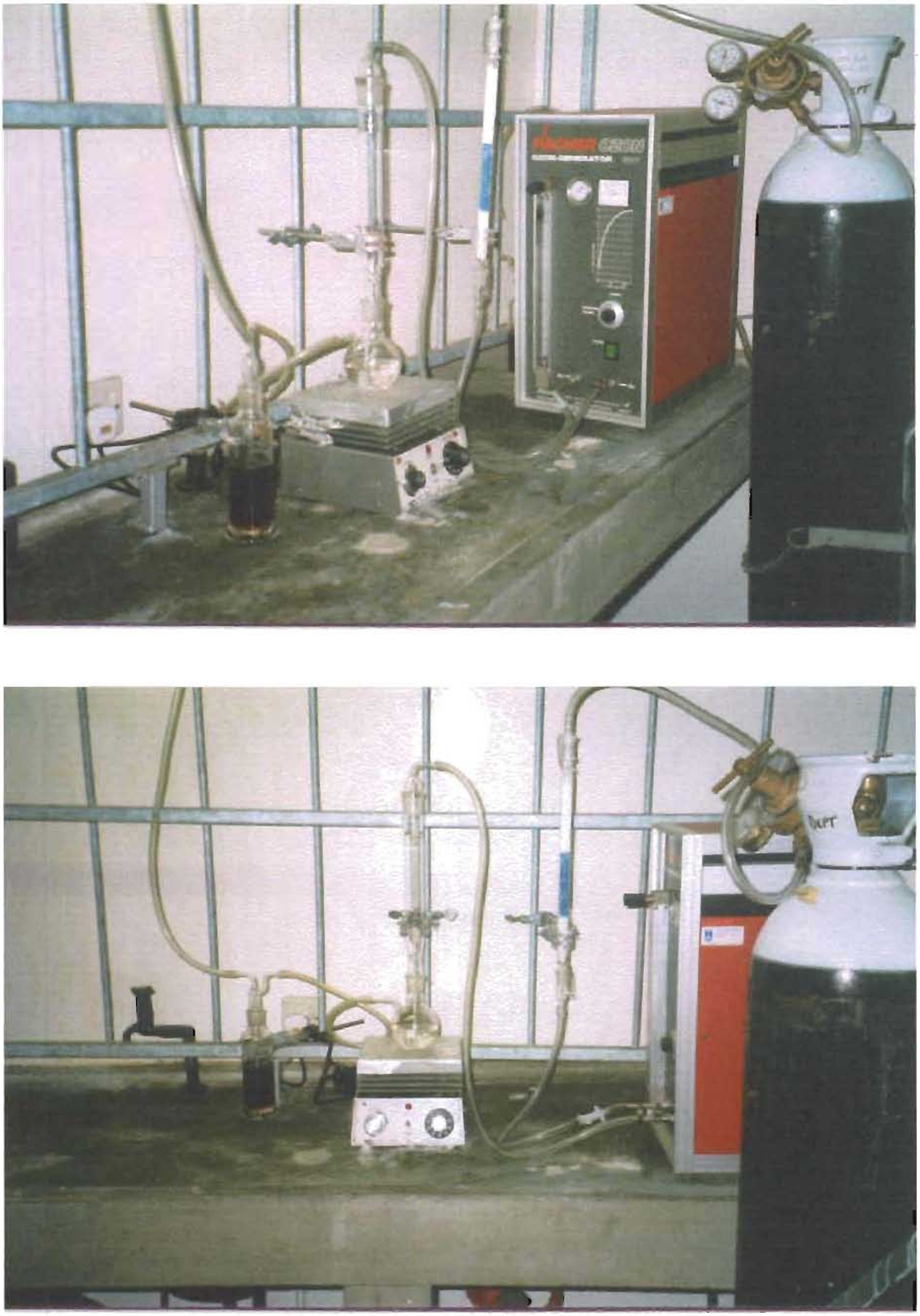


Figure 5: Photographs of the Ozonation Apparatus

CHAPTER 3: EXPERIMENTAL METHODOLOGY

3.1 Microwave Plasma Experiments

A number of experiments were first carried out in order to optimise the settings or control levels for various parameters. This was particularly necessary in the case of the microwave experiments, as the plasma proved to be very sensitive to gas flow and pressure conditions. Details of the optimisation process are given in section 4.1. The following parameters were considered for the microwave experiments:

gas flow rate;
volume of wax in reaction flask;
vacuum (pressure);
microwave power output;
distance from centre of plasma to wax surface;
reaction time.

The latter two parameters could only be optimised by identifying a measurable change to the wax. The measurement used was the acid value of the wax, determined by wet chemical analysis, as this was the easiest, simplest, and most reliable method. To some extent this presupposed that some change would take place, but some earlier work [75], although unsuccessful [76], had shown that the possibility existed.

The stability of the plasma was dependent on the pressure inside the plasma tube. This in turn was dependent on three of the above parameters - vacuum applied, gas flow, and volume of wax. The wax volume dictated the height of the wax above the frit, and therefore the back pressure inside the plasma tube. Due to small variations in flask height and plasma tube length (the total combined variation was not more than 10 mm), it was found easier to fix the wax volume rather than the depth that the frit was submerged. The back pressure inside the plasma tube is caused by resistance to gas flow resulting from:

the constriction due to the shape of the tube;
the frit, which forces the gas through narrow passages (pores); and
the liquid head of wax through which the gas must pass.

The gas flow from the storage cylinder, and the vacuum pump connected to the exhaust side of the reaction flask (via the traps) counteract these resistances, but at the same time, the concentration of gas inside the plasma tube has to be very low [37,54] in order to achieve plasma formation and hence the required singlet molecular oxygen.

The vacuum was difficult to control precisely, due to imperfectly sealed joints, minor differences in valve openings, etc., but generally had to be in the range 2-6 torr for a plasma to be struck.

Gas flow was eventually standardised at 0.2 dm^3 min^{-1}. A plasma could still be generated at higher flows, but it was found to be more stable at this lower flow rate. Also, higher gas flows caused wax losses due to the vigour of bubbling, splashing wax onto the cool upper surfaces of the reaction flask where it solidified and was no longer available for reaction. With time, this could lower the level of wax to such an extent that the frit was no longer submerged and therefore singlet oxygen contact with the wax became minimal.

Compared with other workers [54,56], much higher microwave outputs were required to maintain a stable plasma. This in turn led to much higher powers being absorbed by the gas. An output of at least 200 W was required to maintain a stable plasma, with reflected power being 60 - 100 W, but usually outputs of 300 - 600 W were used, with reflected powers of 100 - 200 W being recorded

To confirm that the singlet oxygen had a long enough lifetime to react with the wax, an experiment was carried out using the apparatus (except that a cooling bath was substituted for the hotplate) to copy a reaction established in the literature. The reaction of 2,5-dimethyl 2,4-hexadiene with singlet oxygen [77] was successfully carried out, NMR being used to follow this reaction. As the reaction progressed, the methyl proton peak at 1.9 ppm was replaced by a methyl peak at 1.3 ppm. Similarily, the vinyl proton peak at 5.9 ppm was replaced by a peak at 6.4 ppm.

3.2 Ozonation Experiments

These experiments were much more straightforward than the microwave experiments as there were fewer variables to control. These parameters were;

gas flow rate;
spark discharge current;
mass of wax; and
reaction time.

The spark discharge current was based on the equipment manufacturer`s recommendations, while the reaction time was that finally adopted for the microwave experiments. The gas flow rate and mass of wax were also largely based on the microwave experiments, but were both higher. The reason for the higher gas flow rate was to overcome the liquid head of the potassium iodide solution used to reduce the unreacted ozone to oxygen on the exhaust side of the reaction flask.

3.3 Blank Experiments

With every set of experiments performed, 'blank' runs were also carried out. In the case of the microwave experiments, these entailed using the same experimental conditions but with the microwave power switched off. Similarly, ozonolysis blanks were run by keeping the spark discharge current in the 'off ' position. In this manner, any observed effects could be attributed to the gas plasma or ozone, respectively, and no other phenomenon. A few of the microwave experiments were also carried out with the oxygen substituted by argon or nitrogen.

3.4 Wax Analysis

As mentioned previously, the primary method of analysis was the acid value determination, described in Appendix I .Determination of the saponification value was also performed on several samples. This analysis determines the number of acid and ester groups. Like the acid value determination, this is also a wet chemical method, but more complex. The method is detailed in Appendix II. Whilst undertaking the research for this thesis, a modified version of the saponification value determination was developed using microwave heating rather than conventional heating (see section 5.2).

Instrumental techniques such as IR and NMR are not very useful for quantitative determinations of the oxygen-containing groups in waxes as a result of the number of different chain lengths present in the waxes. With a greater degree of computerisation, allowing incorporation of statistical smoothing techniques, calibration of instruments can be achieved. Both FTIR and NIR techniques for measurement of acid values have, in fact, been established [78,79], but are not yet in normal use because of the expense of the equipment, and expertise required to operate it.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Microwave Optimisation Experiments

This group of experiments used one wax, wax A, (see Table 6 in Section 4.2 for details of the waxes), while various parameters were changed. A measurable change was regarded as one which resulted in a difference to the acid value of the wax.

4.1.1 Height of Plasma above Wax

The height was measured from the centre of the microwave beam to the bottom of the reaction flask containing the wax. Originally 260 mm, this was reduced to 200 mm before a measurable change to wax A was achieved. The reason for the change occurring was thought to be due to the lifetime of the singlet oxygen being so short that the concentration of singlet oxygen with distance (time) rapidly decreased.

4.1.2 Flow Rate / Wax Mass

As discussed in Section 3.1, these two parameters are affected by each other and were therefore optimised simultaneously. In this case, plasma stability was a more important outcome than a change to the wax composition. Several experiments led to the adoption of a wax mass of 30 g and an oxygen flow rate of 0.2 $dm^3 min^{-1}$.

4.1.3 Microwave Power

Plasma stability is also a function of the microwave power applied, but in this instance the power was largely optimised based on changes to the wax composition. An output power of 600 W was adopted as standard. Use of higher power outputs than this led to overheating of the plasma tube and consequent structural failure (melting) of the tube.

Power out (W)	Power absorbed (W)	Acid value change (mg KOH/g)
300	200	-1.1
600	420	-2.1

4.1.4 Reaction Time

Reaction time was increased in steps from 20 min to 60 min. Due to heating effects it was deemed prudent not to run the experiments for longer times than this.

Time (min)	Acid value change (mg KOH/g)
20	-1.5
30	-2.1
60	-3.1

4.1.5 Optimum Settings

The above experiments resulted in the adoption of the following settings for the subsequent microwave experiments:

Height of centre ofplasma above reactor flask bottom	200 mm
Oxygen flow rate	0.2 $dm^3 min^{-1}$
Wax mass	30 g
Microwave power output	600 W
Reaction time	60 min

4.2 Microwave Oxidation Experiments

Using the optimum settings, several different waxes (see Table 6), were subjected to reaction with singlet oxygen. The results are summarised in Table 7, *each result being the average of at least three experiments compared with a blank experiment.*

Table 6: Waxes used in experiments

Wax	Trade name	Manufacturer	Description	Acid value (mgKOH/g)	Congealing pt. (°C)	Penetration @ 25°C (mm x 10^{-1})
A	Sasolwaks A7	Schümann Sasol	Oxidised FT	28.1	92	8
B	Vestowax C60	Hüls	Oxidised FT	26.8	88	8
C	Paraflint H5	Schümann Sasol	FT	0	101	<1
D	AC629	Allied Chemicals	Oxidised polyethylene	14.3	92	5
E	Paraflint A600	Schümann Sasol	Saponified FT	12.1	105	<1
F	LE112	Leuna	Polyethylene	0	101	3
G	Waksol A	Schümann Sasol	FT	0	35	>120

Table 7: Experimental Results

Wax	Acid value change (mgKOH/g)*
A	-2.9
B	-0.7
C	0
D	+0.5
E	-1.0
F	0
G	0

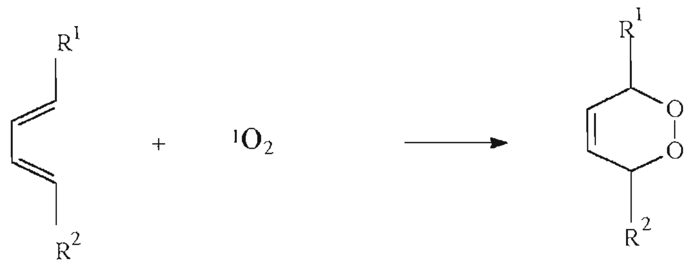
*Average of at least three experiments compared with at least one blank experiment.

What is notable about the results is that only the oxidised waxes showed any measurable changes due to treatment with singlet oxygen. Unexpectedly, the oxidised FT waxes all showed decreases in acid value, while the oxidised polyethylene wax, D, showed a small increase. The other waxes showed no differences.

It should first be explained why singlet oxygen was considered to be a possible oxidant of waxes, and why waxes already containing oxygen functional groups might behave differently.

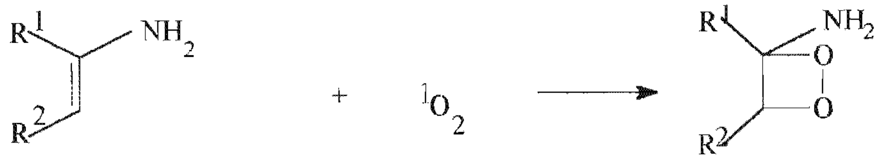
Three types of reaction for singlet oxygen have been described by Frimer [37]. Briefly, these are:

(i), *The singlet oxygen Diels-Alder reaction.*These reactions are analogous to the well-known Diels-Alder cycloaddition reaction in which a conjugated diene reacts with a dienophile to form a cyclic compound. In the singlet oxygen version, the singlet oxygen itself is the dienophile, and upon reaction with a diene, forms an endoperoxide, as shown below:



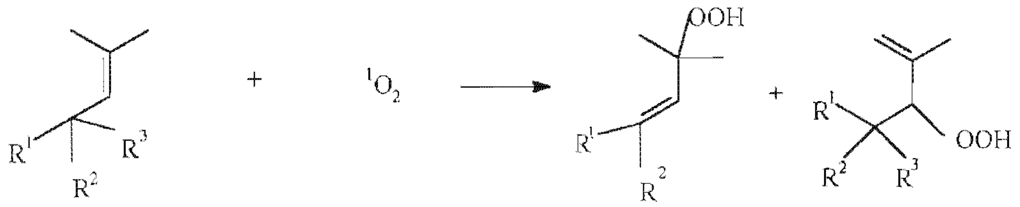
The endoperoxide could then break down to a hydroxyketone or possibly a furan.

(ii) *The singlet oxygen dioxetane-forming reaction.* In this reaction, the singlet oxygen reacts with a heteroatom activated double bond (most commonly in enamines, enol ethers, and vinyl sulphides), to form a dioxetane, as shown below:



Most dioxetanes are thermally unstable, breaking down to carbonyl fragments, although more bulky, rigid groups attached to the dioxetane functionality can render the dioxetane more stable.

(iii) *The singlet oxygen ene reaction.* A double bond combines with the singlet oxygen to form an allylic hydroperoxide in this reaction. Note that the double bond shifts to a neighbouring position:



The hydroperoxides formed can undergo several reactions, but under the conditions of the experiments carried out above, homolysis to the alkoxy radical is the most likely, leading to products similar to the free radical oxidation process, i.e. alcohols, ketones, acids and esters.

A number of mechanisms have been proposed for each of the reactions shown above (summarised by Ogryzlo in [54], but see also Frimer [37]) and, of course, a broader spectrum of subsequent reactions is also possible. However, the subsequent reactions are dependent on the prevailing experimental conditions, the predominating ones being an oxidising atmosphere and a relatively high temperature.

Given our knowledge of the wax structure, specifically that there are relatively few double bonds with few or no activating groups, it was thought that the singlet oxygen ene reaction was that most likely to take place.

Wax F, a fully saturated polyethylene wax, was not expected to undergo any reaction, as it does not have any of the desired structural characteristics for reaction with singlet oxygen.

This does not mean that polyethylene cannot undergo reaction with singlet oxygen, and a number of investigators have studied the role of singlet oxygen on polymer degradation (see, for example, [80, 81]). Studies investigating singlet oxygen as a surface modifier of (solid) polymers have also taken place [82,83].

Waxes C and G are slightly unsaturated FT waxes and it was hoped that these waxes would undergo reaction with singlet oxygen. The fact that the level of unsaturation is low, approximately 0.7 moles of double bond per mole of wax (more usually expressed in terms of a *bromine value* (see Section 6.6), may explain why no measurable change in acid value due to reaction with singlet oxygen was observed. Wax C also has very low levels of branching, FT waxes being renowned for their linearity, and most of the singlet oxygen reactions described [37, 77], involve the presence of a tertiary carbon in the molecule. Wax G has a much higher degree of branching and also has much shorter chain lengths. Statistically, this should increase the probability of suitable "ene" structures being present in the wax, but this is not shown by the results.

The remaining waxes are all oxidised waxes. It was thought that the presence of oxygen-containing functional groups might enhance the reactivity of the wax towards the singlet oxygen. The results of the experiments with the three oxidised FT waxes were therefore viewed with some surprise. Initially, it was hypothesised that the acids were being converted to esters, but the saponification values of the singlet oxygen-treated waxes also showed reductions (see Table 8). Conversion of acids to esters should have resulted in the saponification values being essentially unchanged (since the saponification value is equal to the sum of the ester and acid values).

Table 8: Saponification values

Wax	Saponification value (mgKOH/g)	
	Blank	$^1O_2$-treated
A	59	55
B	54	48
E	31	29

Work done at Schümann Sasol [84] has shown that light acids may be lost by distillation, treatment with a flow of an inert gas (nitrogen) at high temperature [85], or even by elevated temperature alone, and thus it was suspected that the high temperature plasma was acting as a carrier for the light acids, resulting in the lower acid value of the remaining wax. This is despite the wax temperature being measured to be no more than 130°C. This hypothesis was tested by treating wax A with an argon plasma. Using similar parameters and conditions to the oxygen experiments, the argon plasma gave the same results as the oxygen plasma, i.e. a reduction in acid value. While it is known that excited states of argon exist [56], it is extremely unlikely that an argon compound could have been formed at the expense of the acid groups, so this was taken to be conclusive proof that the hot plasma was flushing the light acids out of the liquid wax.

This in itself does not prove that no reaction with singlet oxygen took place. The initial optimisation experiments regarding distance of the wax from the plasma possibly provide greater proof, in that they showed that the further away the wax was from the plasma, the smaller the decrease in acid value was found to be, but no positive effect (increase in acid value) was seen.

Thus the evidence is strong that no reaction took place between the singlet oxygen and the oxidised FT waxes. This should still not be taken as conclusive, as no attempts were made to measure hydroxyl or carbonyl groups, which would form first if the singlet oxygen ene reaction led to the hydroperoxide. Measurement of these functional groups by wet chemical techniques is not very precise, experience at Schümann Sasol suggesting that repeatabilities of less than 5mgKOH/g are not attainable. Qualitative insrumental techniques have not yet been developed which are suitable for analysis of oxidised waxes. However, practical experience has shown that if hydroxyl or carbonyl groups had formed, acids and esters would have also been formed within the time that the oxidations took place.

In contrast to the above experiences, the oxidised polyethylene wax, wax D, did show that oxidation by singlet oxygen had taken place. While the change was small, and slow compared to standard oxidation processes, it is a significant change. The molecular mass of this polyethylene wax is almost double that of the FT waxes, and therefore the presence of light, volatile acids in this wax is less prevalent. In terms of structure, the polyethylene waxes are also more branched, and together with the existing oxygen functional groups, the characteristics desirable for, presumably, the singlet oxygen "ene" reaction, have been achieved.

In summary, only the oxidised polyethylene wax underwent reaction with singlet oxygen, resulting in a slightly more oxidised wax. This is most probably because of the physical structure of the wax, which better fits the characteristics of compounds known to react with singlet oxygen.

4.3 Ozonation Experiments

Little was required in the way of optimisation of the ozonolysis experiments because of the much simpler ozone generation technique and adoption of an experimental setup as similar as possible to that used for the microwave experiments. The settings of the ozone generator (current, gas pressure) were based on the recommendations of the equipment manufacturer. The gas flow was chosen to be as similar as possible to that used in the singlet oxygen experiments, without causing problems with the experimental setup. The conditions settled upon were:

spark discharge current:	0.3 A
gas pressure:	0.95 bar
gas flow:	40 $dm^3\ h^{-1}$ (0.66 $dm^3\ min^{-1}$),
mass of wax:	50 g

As can be seen, the gas flow rate was somewhat higher than the microwave experiments (0.2 $dm^3\ min^{-1}$), this being a result of operating at atmospheric pressure rather than under reduced pressure. The higher gas flow also helped overcome the back pressure of the ozone scrubber. The latter consisted of a solution of buffered potassium iodide (composition: 20 g KI, 7.3 g Na_2HPO_4, and 3.5 g KH_2PO_4, per litre of water) into which the exhaust gas from the reaction vessel was vented. The ozone is decomposed by the reaction:

$$O_3 + 2KI + H_2O \rightarrow I_2 + 2KOH + O_2$$

The mass of wax used was increased to 50 g, but reaction time was maintained at one hour.

As for the microwave experiments, a 'blank' run was performed by passing oxygen through the ozone generator with the power to the spark discharge in the 'off' position, i.e. with no current, then, as normal, bubbling through the wax. The change in acid value reported is therefore the difference between the results obtained for experiments with ozone and the blank experiment with the same wax.

The results of the experiments are summarised in Table 9, below. The experiments show that substantial increases in acid values were achieved by ozonolysis. The two waxes, C and F, which showed the least amount of oxidation, are both relatively high molecular mass waxes with very little unsaturation and no functional groups. The other waxes do not appear to show any further relationship between structure and degree of oxidation, but they all have more tertiary positions than waxes C and F, which may account for their greater extent of oxidation.

Table 9: Results of ozonolysis experiments

Wax	Acid value change (mgKOH/g)*
A	+7
B	+12
C	+4
D	+5
E	+6
F	+4
G	+10

*Average of at least two experiments compared with a blank experiment

The majority of ozonolysis reactions [86] are the result of electrophilic attack by ozone at an electron-rich centre such as an unsaturated bond with its π orbital system. Certain heteroatom sites, as well as saturated compounds with electron-rich σ bonds, are also liable to attack by ozone. Thus waxes with double bonds (e.g. wax G), oxygen-containing functional groups (the oxidised waxes A, B, D, and E), or with tertiary carbons, all react with ozone.

The experimental evidence indicates that ozone is a strong enough electrophile to oxidise even waxes C and F, which have very few unsaturated or tertiary positions.

A few mechanisms have been suggested for ozonations under different conditions. A radical mechanism is proposed for gas phase reactions and is basically similar to the classical free radical mechanism for normal oxidation described earlier (see Hellman [87]).

$$\mathrm{RH} + \mathrm{O_3} \rightarrow \mathrm{R}\bullet + \bullet\mathrm{OH} + \mathrm{O_2} \rightarrow \text{Hydroperoxides} + \text{carbonyls} + \text{hydroxyls}$$

Under the strong oxidising conditions, the hydroperoxides break down to form the other oxygen functional groups as per Semenov's 1935 [18] mechanism.

4.4 Conclusions

The results show that ozonolysis is a much more effective means of wax oxidation than th use of singlet oxygen. In most cases, the latter method did not appear to cause any oxidation of the substrate, and in the one example where oxidation did occur, the extent of oxidation was small compared to standard oxidation techniques.

However, it could be asked if the comparisons are fair, given that the gas flows in particular, were somewhat different. In industrial practice, the significant value is not the gas flow as such, but the gas flow *per unit mass of wax*. If we convert the experimental gas flows to the units of ml (oxygen) per minute per gram of wax, we see the following:

singlet oxygen	6.7 ml/min/g
ozonolysis	13.2 ml/min/g
normal oxygen	1.0 ml/min/g (typically)

This shows that most oxygen was supplied during ozonolysis, but it cannot be concluded that this, therefore, is the reason for its more pronounced oxidative ability. This is demonstrated by the fact that normal oxidation works much more effectively than the singlet oxygen, despite the oxygen supply for normal oxidation being less than 20% of that supplied during the singlet oxygen experiments. Also of relevance is the temperature and the wax itself. If we ignore normal oxidation (where reactor design can have an effect on required gas flow [88-91]), ozone not only oxidised the waxes at more than double the rate of the singlet oxygen, where the latter was effective, it also oxidised waxes at a high rate when singlet oxygen had been completely ineffective. In all cases the wax temperatures were much the same, and the same reactor was utilised.

It should be noted that for normal oxidation doubling the gas flow rate would almost definitely **not** double the oxidation rate, unless the initial flow rate was too low. For a particular reactor design (and capacity) and process conditions, an optimal gas flow can be found. Using gas flows above this optimum is uneconomical and can even have a detrimental influence on the oxidation rate.

Thus, it can be concluded that ozonolysis is the more effective of the two expeimental oxidation methods studied. It may also be more efficient than the standard technique (see Section 4.5 below).

The use of microwaves to produce singlet oxygen proved to be a very convenient and fairly reliable method. The substrate could be reacted directly with gas phase singlet oxygen without recourse to additional chemical treatments.

4.5 Suggestions for Further Work

From the commercial point of view, the ozonolysis route provides a possible alternative to current processes. The procedure does need to be refined for possible scaling up, and both the economic and safety aspects need to be fully explored before any industrial-scale operation could be considered. The work performed for this dissertation shows that this could be a promising option, however.

On the other hand, further work should investigate the reasons for singlet oxygen reaction with only the oxidised polyethylene wax. A wider range of such waxes would need to be studied and a better definition of the structure of the waxes may be required to provide more information why singlet oxygen reacts with this type of wax in particular

Further investigations could be made on the interactions of other gases in an excited state with the molten waxes. Using the apparatus described here, plasmas of nitrogen and carbon monoxide (see Section 5.4) were also generated, but a study of the interaction of these species with waxes was not attempted in this work.

CHAPTER 5: OTHER MICROWAVE EXPERIMENTS

5.1 Introduction

One of the secondary objectives of this work was to explore further the use of microwaves in chemistry.

Probably the widest use of microwaves in chemistry has been their use as an alternative source of heat. Section 5.2 describes the development of an analytical method in which a microwave oven replaces conventional heating.

Section 5.3 describes a simple experiment which demonstrates the "selectivity" of microwaves.

A short account of further microwave-generated plasma work is given in Section 5.4, and Section 5.5 draws some conclusions about the use of microwaves in chemistry.

5.2 Development of Method for Determination of Saponification Value using Microwave Oven

The largest area of microwave use in chemistry has been to replace conventional heating methods. The most important attribute of the microwave technology is its ability to heat faster and more efficiently (heating the material directly, not via container or other environment).

One of the more important analyses performed on oxidised waxes is the determination of saponification value. A method for the determination of saponification values of synthetic and natural waxes is described in the ASTM (American Society for Testing and Materials) Standards [92], and is widely used in the wax industry. Essentially, the method involves the saponification of the acid and ester groups of the wax by potassium hydroxide, brought about by refluxing the wax in a xylene/ethanol mixture containing an excess of KOH. The residual KOH is titrated with hydrochloric acid. The saponification value is derived by subtracting the volume of HCl required to neutralise the excess KOH left in the sample solution, from the volume of HCl required to neutralise the KOH in a blank solution (i.e. no wax). The method calls for at least three hours of heating under reflux (see Appendix II).

Sasol [93], a wax manufacturer, subsequently modified the method by adopting a different solvent, 2-methoxyethanol (often called by its trade name, methyl Cellosolve), to replace the ethanol. This resulted in the reflux time being reduced to a minimum of 45 minutes.

Note that both reflux times are the minima required and are usually adequate for most of the natural and FT waxes, but some of the polyolefin waxes require much longer times. A copy of the Sasol method is reproduced in Appendix II.

Because of the long analysis time, this method was considered to be a good candidate for the application of microwave technology. Another consideration was that the solvent used is expected to have a significant dielectric loss tangent [94] and thus be a good microwave energy absorber.

Initially, it was proposed merely to replace the heating mantle normally used with a microwave oven and retain the reflux apparatus. While this was feasible for a single sample apparatus, it was deemed too hazardous and complex for a multiple-sample arrangement, as the possibility of microwave leakage became too great. It was therefore decided to contain the sample, with solvent, in a closed pressure vessel.

A sample of such a vessel, manufactured by CEM [95], was kindly lent by Microsep [96]. In order to prevent the vessel being over-pressurised (although the vessel is fitted with a bursting disc to prevent such incidents), square-wave power application was used. In this mode, the microwaves are provided in pulses of a selected length. A 1 kW oven, modified by Pougnet [97], was used for these experiments [98].

After some preliminary experiments using water, a pulse time of four seconds was chosen. One gram samples of wax, in 30 ml of KOH in methyl Cellosolve, were then heated for different times before titration to obtain the saponification value. These results were then compared to the value obtained by the traditional method. An optimum time for the microwave heating was thus obtained. It was found that four minutes was sufficient to saponify the (FT) wax fully. It was found to be necessary to cool the vessel in cold water for two minutes, before it could be safely opened. After the initial titration, the sample was heated for another minute, to ensure the sample had been fully saponified. The final titration value was then obtained, and the saponification value calculated.

This method was then used to determine the saponification values of a number of waxes whose values had previously been determined by the conventional method. As there was excellent agreement between the results, more vessels were purchased and the method developed for doing four samples simultaneously. This is typically the number of samples done at any one time by the analysts in the Schümann Sasol [99] Service (quality control)

Laboratory. A new oven was also obtained, and the controls modified in the same fashion as that used originally. The apparatus is shown in Figure 6.

As expected, the heating time had to be increased due to the greater volume of liquid (in total) absorbing the microwave power. While the pulse time was maintained at four seconds, the heating time was increased to 15 minutes before the first titration, and another 5 minutes before the final titration. The vessels were cooled in cold water for about three minutes before they could be safely opened for titration.

The titration values of two different waxes were then determined a sufficient number of times by both the conventional and microwave methods so that statistical analysis of the results could be performed. The results are shown in Table 10 (overleaf).

The statistical method used was a hypothesis test. The null hypothesis [100] was that the difference between the means of the two different methods is zero, i.e., the means are the same. A summary of the statistical tests for both waxes is shown in Table 11.

Table 11: Summary of hypothesis testing

Paraflint A1	Paraflint A2
Null hypothesis: population means are equal	Null hypothesis: population means are equal
Confidence interval, $\alpha = 0.1$	Confidence interval, $\alpha = 0.1$
2- tailed test, 39 degrees of freedom	2- tailed test, 42 degrees of freedom
$t = 1.685$	$t = 1.645$
If $t > 1.685$, or $t < -1.685$, then reject null hypothesis.	If $t > 1.645$, or $t < -1.645$, then reject null hypothesis.
Standard deviation of difference between means, $s_{c-m} = 0.336$	Standard deviation of difference between means, $s_{c-m} = 0.318$
$t = \frac{\bar{x}_c - \bar{x}_m}{s_{c-m}} = -0.357$	$t = \frac{\bar{x}_c - \bar{x}_m}{s_{c-m}} = 0.314$
Null hypothesis is accepted.	Null hypothesis is accepted.

The conclusion reached was that the microwave method gave the same results as the conventional method. Repeatability and reproducibility were at least as good as the ASTM method

Appendix II contains reprints of the ASTM and Sasol methods as well as the microwave method as adopted by Schümann Sasol [101].

This work was presented in poster form at the International Conference on Microwave Chemistry, held in Prague from the 6th to the 11th September, 1998. A copy of the abstract is included in Appendix III.

Table 10: Saponification value determination results (mgKOH/g)

	Paraflint A1		Paraflint A2	
	Conventional	Microwave	Conventional	Microwave
1	47.70	49.67	32.22	30.23
2	47.32	48.25	33.90	31.14
3	49.19	48.99	32.00	30.45
4	48.53	50.46	32.32	31.25
5	47.64	48.95	32.55	30.63
6	48.88	48.05	32.99	32.89
7	47.47	48.98	31.68	33.69
8	47.50	47.86	30.46	31.45
9	48.67	48.90	32.43	32.78
10	50.62	47.49	32.74	33.13
11	49.93	47.64	31.19	32.13
12	50.60	49.14	32.90	32.96
13	49.59	49.26	32.13	31.34
14	50.59	49.91	32.72	32.99
15	47.40	47.70	30.57	31.05
16	47.87	48.87	31.48	31.55
17	47.25	48.22	33.18	31.95
18	50.51	47.54	33.18	31.18
19	48.46	49.74	30.83	32.64
20	47.42	48.96	30.47	33.77
21		49.90	30.62	32.41
22				32.31
23				30.15
	$n_c = 20$	$n_m = 21$	$n_c = 21$	$n_m = 23$
	$\bar{x}_c = 48.66$	$\bar{x}_m = 48.78$	$\bar{x}_c = 32.02$	$\bar{x}_m = 31.92$
	$s_c = 1.254$	$s_m = 0.8728$	$s_c = 1.018$	$s_m = 1.082$

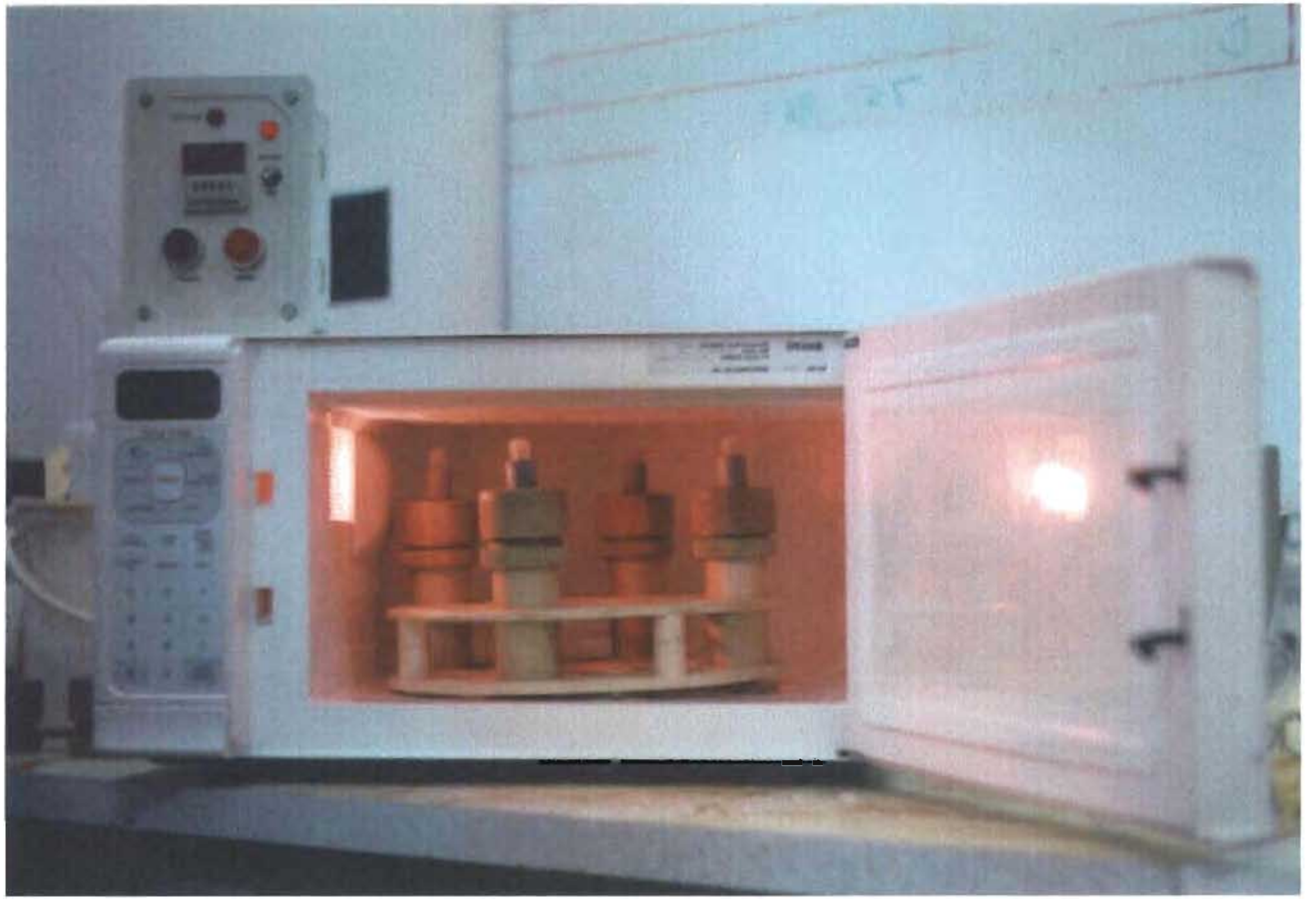


Figure 6: Microwave Apparatus for the Determination of Saponification Values

5.3 Simple Experiment to Demonstrate "Selectivity" of Microwaves

The ability of microwaves to heat a substance largely depends on certain fundamental properties of the substance itself. In simple terms, the substance must contain molecules with permanent or induced dipole moments. Application of an electric field exerts a force on the dipoles causing the molecules to rotate until they are aligned. When the electric field is reversed, thermal agitation returns the molecules to a disordered state with a small release of thermal energy. At microwave frequencies, alignment and relaxation occurs in the order of 10^9 times per second and the thermal energy released results in rapid heating of the substance. The rate of heating is related to the dielectric constant (which describes the ability of the substance to undergo polarisation) and dielectric loss of the substance (the efficiency with which the energy of the electromagnetic raddiation can be converted into heat).

Application of an electric field can also induce a current when the substance is a conductor. In this case, heating of the substance is due to resistance to current flow.

A fuller explanation is given in Mingos [102].

Hydrocarbons, having no dipoles, are therefore almost completely transparent to microwaves. The waxes containing oxygen functional groups on the other hand, absorb microwave energy because of their polar character. This is demonstrated by the following experiment.

Two "candles", approximately 2 cm diameter and 10 cm long, were prepared. One was formed using normal candle wax (medium melting point FT wax), and the other from oxidised FT wax. The candles were then suspended in the waveguide of the apparatus used for the singlet oxygen experiments. A small amount of power (50 W) was applied. After 10 minutes, no effect was seen on the normal candle, but when the experiment was repeated on the oxidised wax candle, a "hole" was soon melted in the candle. This is graphically illustrated in Figure 7 overleaf. The normal candle wax and the oxidised wax are labelled H2 and A28 respectively.

5.4 Microwave-Induced Plasmas

As mentioned in Section 1.4, gas plasmas are used as a means of generating steady-state concentrations of atoms and unstable molecules for spectroscopic measurements. While inductively-coupled plasmas (ICP) using radio frequencies are more commonly used, microwave-induced plasmas (MIP) are reported to have some advantages (see Matousek *et al*

H2 = hydrocarbon wax
A28 = oxidised wax

Figure 7: Demonstration of Microwave Selectivity

[56]). For spectroscopic work, argon and helium are the most commonly used gases in MIP. Nitrogen, common in ICP, is seldom used in MIP.

It was reported in Section 4.2 that an argon plasma was used to verify that observed effects were due to plasma heating and not due to active species in the plasma. A nitrogen plasma was also generated to test this, but problems were experienced. It appears that the nitrogen plasma is much hotter than both the oxygen and argon plasmas, as within twenty minutes the plasma tube began to suffer from "pinholing". This phenomenon is due to a very localised part of the (glass) plasma tube becoming hot enough to soften. The low pressure inside the tube causes this piece of glass to be drawn into the tube, until the glass film is so thin that it ruptures. This, of course, results in loss of the low pressure inside the tube, and hence, the plasma is also lost.

Out of curiosity, a few experiments were carried out to establish a carbon monoxide plasma. Stable plasmas were obtained under much the same conditions as for the oxygen plasma. Work has been reported on the use of microwave-induced plasmas with carbon monoxide/hydrogen mixtures for vapour deposition of diamond films (see Lee *et al.* [103]).

5.5 The Use of Microwave Technology in Chemistry

Microwave technology began with its use in the late nineteen-thirties in Radar, a detection technique for locating and tracking physical objects. Initially used for detecting aircraft and, later, ships, nowadays it can be used for tracking even smaller objects and also weather fronts. Radar uses frequencies from 1 to 30 GHz, corresponding approximately to wavelengths of 25 to 1 cm, this covering most of the microwave range.

The ability of microwaves to heat water was recognised quite early, with commercial microwave heating devices appearing in the nineteen-fifties.

In the early 'sixties, the use of microwaves for spectroscopic purposes started to gain currency. Research into the use of microwave-induced plasmas took place in the early 'seventies, but it was only in the 'eighties, that the use of microwave heating for chemical reactions began to be explored. One of the first to be published, by Gedye *et al.* [104], appeared in 1986. This was probably entirely due to the mass marketing and production of domestic microwave ovens, whose price range was within the grasp of many consumers, in the early 'eighties.

Since then, the use of microwaves in chemistry has expanded enormously both in depth and breadth. This is demonstrated by the large number and variety of topics covered at the recent International Conference on Microwave Chemistry [105]. A recent review by Strauss [106] gives a taste of the future possibilities for microwaves in the development of environmentally benign processes for laboratory-scale organic synthesis and for the production of fine chemicals and pharmaceuticals.

Clearly, there are vast unexplored regions with respect to the use of microwaves in chemistry, and the next decade is likely to see further growth in this field.

CHAPTER 6: GLOSSARY OF TERMS USED BY WAX CHEMISTS

6.1 Introduction

A number of terms are used by chemists to define the properties of a wax, many of which are peculiar to the industries using waxes. The following sections explain these terms, describe how they are measured, and why they are relevant. Reference [107] is a general reference covering most of these descriptions. References are also given to the analytical methods approved by the ASTM or Institute of Petroleum (IP), as well as Schümann Sasol (SS).

6.2 Melting Points

Wax chemists describe waxes by a number of different types of melting point, which can differ considerably, depending on the wax. Four types of melting point are typically used in the wax industry:

(a) *congealing point*: the temperature at which a wax, allowed to cool under prescribed conditions, ceases to flow [ASTM D938-86, SS006-98]. This melting point is most important to candle manufacturers, wax blenders and manufacturers, as it is a simple method which gives good information for storage and processing of the wax.

(b) *softening point*: the temperature at which a wax disc, being heated up under prescribed conditions, deforms to a specified extent [ASTM D3461-85, SS016-98]. This test is used in place of the congealing point when the wax has a high-enough viscosity that the determination of congealing point becomes difficult. The polish industry generally uses the softening point to describe melting characteristics.

(c) *dropping point* or *drop melting point*: the temperature at which a wax, being heated up under prescribed conditions, becomes sufficiently fluid for a drop of liquid wax to separate from the sample by force of gravity [ASTM D3954-80, SS021-98]. Commonly used by a number of industries, being one of the first automated methods.

(d) *cloud point*: the temperature at which the high molecular weight component of a molten wax, being cooled under prescribed conditions, begins to crystallise [ASTM D2147, SS012-98]. This measurement is important to polish and coatings manufacturers, as it gives information regarding the transparency of the applied product. Wax manufacturers can also use it to determine efficiency the of separation processes (e.g. distillation).

Table 12 shows the values of these variously defined melting points for a selection of waxes.

Table 12: Melting points of waxes (°C)

Wax	Description	Congealing pt.	Softening pt.	Dropping pt.	Cloud pt.
LE114[a]	PE wax	102	115	115	107
LE253[a]	Oxidised PE wax	92	107	106	99
H2[b]	FT wax	97	110	112	103
A1[b]	Oxidised FT wax	88	98	99	92
A2[b]	Saponified FTwax	89	105	107	95

[a]: Products of Leuna Polymer GmbH

[b]: Products of Schümann Sasol SA (Pty) Ltd

6.3 Physical Characteristics

The two most important physical characteristics of waxes are hardness and colour. The former has an important role in the intended application of the wax. In polish and ink applications, a hard wax is desirable for improved resistance to surface damage, but polishes should not be so hard that application to the surface, or buffing, becomes difficult. Candles need to be hard enough to retain their shape, but not so hard that they become brittle.

Although colour does tend to be more important from the aesthetic point of view, in applications such as inks, coatings, and textiles, poor wax colour can cause problems with the final product.

The standard measure of hardness is needle penetration.

(a) *penetration*: the depth, in tenths of a millimeter, to which a needle, of specified shape and weight, penetrates a wax under prescribed conditions of force, time, and temperature. The temperature of the measurement is reported (25°C being the most commonly used temperature, but harder waxes may also be reported at 65°C) [ASTM D1321-76, SS007-98].

Cone penetration, in which the needle is replaced by a cone of specified shape and weight, is used for soft waxes and polishes.

(b) *Saybolt colour*: a number related to the height of a column of liquid wax, the colour of which is matched to a standard [ASTM D156, SS015-98].

(c) *ASTM D1500 colour*: a number related to the colour of a specified cross-section of liquid wax, matched against a series of standards [ASTM D1500, SS015-98].

The Saybolt colour is normally used for the "water white" waxes that look like water when molten, while the D1500 scale caters for the darker, typically oxidised, waxes. There is a small area of overlap between these scales. Another scale, the *Gardner* colour, exists for extremely dark coloured products, but is seldom used in the wax industry. Tables 13 and 14 show some typical values of hardness and colour.

Table 13: Penetration values of waxes (mm x 10^{-1})

Wax	Type	penetration @ 25°C	penetration @ 65°C
H2[a]	FT wax	1	21
A1[a]	oxidised FT wax	7	88
J324[b]	saponified FT wax	3	75
AC629[c]	oxidised PE wax	5	40
LE114[d]	PE wax	2	13

Table 14: Colours of waxes

Wax	Type	Saybolt colour	D1500 colour
H2[a]	FT wax	+24	-
A1[a]	oxidised FT wax	-15	1.0
A2[a]	saponified FT wax	-	2.0
AC629[c]	oxidised PE wax	-	1.0
LE114[d]	PE wax	+29	-

[a] Product of Schümann Sasol SA (Pty) Ltd

[b] Product of Hüls AG

[c] Product of Allied Chemicals

[d] Product of Leuna Polymer GmbH

6.4 Functional Group Analysis

The only functional groups of importance to wax users, and the only two normally measured, are the acid and ester groups.These measurements are normally only performed on oxidised waxes, being of importance to polish and emulsions manufacturers, as they give indications of emulsifiability and solvent compatability.

(a) *acid value* or *number*: the number of milligrams of potassium hydroxide required to neutralise the organic acids in one gram of wax [ASTM D1386-85, SS023-98].

(b) *saponification value* or *number*: the number of milligrams of potassium hydroxide required to neutralise the organic acids and saponify the organic esters in one gram of wax [ASTM D1387-89, SS023-98]. This is also sometimes called the neutralisation value.

Subtracting the acid value from the saponification value, gives the *ester* value. Table 15 shows some typical values of these analyses.

Table 15: Acid , saponification and ester values of waxes (mgKOH/g)

Wax	Type	Acid value	Sap. value	Ester value
H2[a]	FT wax	0	0	0
A1[a]	oxidised FT wax	28	56	28
A2[a]	saponified FT wax	12	32	20
AC629[b]	oxidised PE wax	15	32	17
LE114[c]	PE wax	0	0	0

[a] Product of Schümann Sasol SA (Pty) Ltd

[b] Product of Allied Chemicals

[c] Product of Leuna Polymer GmbH

6.5 Oil Content

This measurement is of no relevance to oxidised waxes, but is extremely important to candle, hot melt adhesive, and coatings manufacturers, where it can be used to gauge suitability for use.

Oil content, or *MEK solubles content*: the amount of oil or fluid present in a wax (actually the amount of wax soluble in methyl ethyl ketone (MEK) at -32°C) expressed as a percentage by weight [ASTM D721-87, SS024-98].

A more powerful solvent, methyl isobutyl ketone (MIBK), can be used for the same test, giving a higher value than the MEK oil content. This is typically only used when the MEK solubles are known to be very low. The values for some waxes are shown in Table 16.

Table 16: MEK solubles contents of waxes (mass %)

Wax	Type	MEK solubles
M3C[a]	FT wax	2.7
M8[a]	Petroleum wax	1.5
C80[a]	FT wax	0.2
NS 120/125[b]	Petroleum wax	0.3
NS 155/160[b]	Petroleum wax	0.2

[a] Product of Schümann Sasol SA (Pty) Ltd

[b] Product of Nippon Seiro Co

6.6 Bromine Value

The bromine value, or number, is also only used in connection with unoxidised waxes. It is of interest because it can indicate reasons for certain physical and chemical characteristics, such as colour and chemical reactivity.

Bromine value: a measure of the degree of unsaturation in the wax, expressed as the number of grams of bromine which are consumed by a 100 g sample of wax [IP 129/64, SS018-98].

The measurement of this value is typically done to determine the effectiveness of wax hydrogenation processes.Values are shown in Table 17.

Table 17: Bromine values of some waxes (gBr/100g)

Wax	Hydrogenated	Bromine value
H1	yes	0.1
H8	no	0.6
H5	no	4.5
Waksol A	no	14.0

All the above are products of Schümann Sasol SA (Pty) Ltd.

Few other terms are peculiar to the wax industry, and many of the other techniques used are also common to other industries. These include gas chromatography, gel-permeation chromatography, thermogravimetric analysis, and differential scanning calorimetry.

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APPENDICES

APPENDIX I: Acid Value Determination

APPENDIX II: Saponification Value Determination

APPENDIX III: Abstract of Microwave Saponification Value Method Development Poster, presented at International Microwave Chemistry Conference, Prague, Sept. 1998.

APPENDIX I: Acid Value Determination

16 DETERMINATION OF THE ACID VALUE OF OXIDISED WAXES

16.1 SCOPE

This method describes a procedure for determining the acid value of oxidised waxes.

16.2 SIGNIFICANCE

The acid value of a wax is the number of milligrams of potassium hydroxide necessary to neutralise the organic acids present in one gram of wax. A high acid value means the wax has a high polarity which means good emulsifiability.

16.3 PRINCIPLE

An accurately weighed sample of wax is dissolved in a measured quantity of pure xylene. After the addition of a measured amount of pure ethanol the sample is titrated with KOH dissolved in methyl cellosolve.

16.4 APPARATUS

16.4.1 250 cm^3 Erlenmeyer flasks

16.4.2 Buret

16.4.3 Hot plate

16.4.4 Scale

16.4.5 Measuring cylinders

16.4.6 Heating mantle

Add 50 cm^3 of xylene and heat on a hotplate until all the wax is dissolved.

Carefully add 25 cm^3 ethyl alcohol and heat to boiling point.

Titrate with 0,1 M KOH in methyl cellosolve solution using phenolphthalein as indicator (V_1).

Do a blank determination (same procedure without wax) in parallel (V_2). If $V_2 > 0{,}1$ cm^3, replace the xylene.

16.8 CALCULATION

$$\text{Acid value, mg KOH/g} = \frac{(V_1 - V_2) \times M_1 \times 56{,}1}{m}$$

Where: V_1 : cm^3 of 0,1 M KOH used with sample
V_2 : cm^3 of 0,1 M KOH used with blank
M_1 : molarity of KOH
m : mass of sample in gram

16.9 REFERENCE

Sasol Analytical Method 2.72/84

16.5.5 0,3 M HCl solution : Dilute 29 cm^3 concentrated HCl to 1 liter with distilled water and standardise according to appendix 1.

16.6 SAFETY

16.6.1 Handle molten wax with gloves and wear safety glasses.

16.6.2 Xylene vapours are harmful and can be absorbed by the skin. Avoid eye and skin contact. In case of skin contact wash with soap and water. In case of eye contact rinse with water and get medical treatment.

Xylene vapours are poisonous and irritate the eyes and respiratory system and cause dizziness.

16.6.3 Methyl cellosolve (ethylene glycol monomethyl ether) forms explosive peroxides when it comes in contact with air. It is also harmful to the skin and eyes. In case of skin and eye contact, wash with water.

Methyl cellosolve is highly flammable and must be kept away from open flames.

16.6.4 During the refluxing of the methyl cellosolve in the presence of aluminium, hydrogen is liberated. Work should thus be carried out in a fume cupboard away from open flames and sparks, as hydrogen is highly flammable and explosive.

16.7 PROCEDURE

Accurately weigh 1 ± 0,1 g wax to the nearest 0,1 mg in a 250 cm^3 Erlenmeyer flask.

16.5 REAGENTS

16.5.1 0,1 M Methyl cellosolve/KOH solution

16.5.1.1 The methyl cellosolve is purified as follows:

For each liter of methyl cellosolve add 6 g aluminium foil, 10 cm^3 distilled water and 10 g KOH. Reflux for 30 minutes for each liter of methyl cellosolve that has to be treated. Bubble nitrogen through the solution to reduce danger of combustion.

Remove the aluminium and distill the methyl cellosolve, discarding the first and last 50 cm^3 for each liter of methyl cellosolve. It is preferable to treat 5 liter of methyl cellosolve at a time.

During the process, hydrogen is liberated and work should be carried out in a fume cupboard away from open flames.

16.5.1.2 Dissolve 6 g of carbonate free KOH in 1 liter of treated methyl cellosolve. Standardise according to appendix 1.

16.5.2 Technical grade xylene

16.5.3 Pure ethyl alcohol

16.5.4 Phenolphthalein indicator (Dissolve 5 g phenolphthalein in 500 cm^3 methanol and dilute to one liter with distilled water.)

APPENDIX II: Saponification Value Detemination

Designation: D 1387 – 89

Standard Test Method for
Saponification Number (Empirical) of Synthetic and Natural Waxes[1]

1. Scope

1.1 This test method covers the determination of the saponification number of synthetic waxes and natural waxes.

1.2 This test method is applicable to Fischer Tropsche, microcrystalline, polyethylene and Montan Ester waxes.

1.3 Certain synthetic waxes, notably copolymers of ethylene, exhibit poor reproducibility when running saponification values. Reproducibility can be improved if cooking time in 7.2 is extended from 3 h to 18–20 h.

1.4 Some oxidized polyethylene and other waxes with a melt temperature above 100°C may give poor reproducibility.

1.5 Some dark-colored (Gardner Color 14) waxes may obscure the color change of the indicator, resulting in poor reproducibility.

1.6 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Document

2.1 *ASTM Standard:*

E 200 Practice for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis[2]

3. Terminology

3.1 *Definition:*

3.1.1 *saponification number*—the number of milligrams of potassium hydroxide required to hydrolyze 1 g of the sample and is a measure of the amount of saponifiable matter present.

4. Significance and Use

4.1 This test method is used to determine the property of ester functionality. Ester functionality determines the utility of the wax as well as being a significant quality control test.

5. Apparatus

5.1 *Analytical Balance.*

5.2 *Boiling Chips,* chemically resistant glass.

5.3 *Burets,* two 50-mL capacity with 0.1-mL graduations.

5.4 *Erlenmeyer Flasks,* 250-mL, alkali-resistant.

5.5 *Hot Plate.*

5.6 *Reflux Condenser.*

6. Reagents and Materials

6.1 *Purity of Reagents*—Reagent-grade chemicals or equivalent as specified in Practice E 200 shall be used in all tests.

6.2 *Hydrochloric Acid Standard (0.5 N).*

6.3 *Phenolphthalein Indicator Solution (10 g/litre)*—Dissolve 1 g of phenolphthalein in 100 mL of USSD3A denatured ethanol or 95 % ethanol.

6.4 *Potassium Hydroxide, Alcoholic Solution (6.6 g/litre)*—Dissolve 6.6 g of potassium hydroxide (KOH) in USSD3A denatured ethanol or 95 % ethanol. Dilute to 1 L with the ethanol.

6.5 *Xylene.*

7. Procedure

7.1 Transfer approximately 1 g of the sample, weighed to the nearest 0.001 g to a 250-mL Erlenmeyer flask.

7.2 Add 40 mL of xylene and a few boiling chips to the flask. Dissolve by heating on the hot plate to the boiling point of xylene. As soon as the wax dissolves, remove from the hot plate and add 50.0 mL of 0.1 N ethanolic KOH solution from the buret. Fit the flask with a reflux condenser and reflux for 3 h using the hot plate.

7.3 Remove the condenser from the flask, add 5 drops of the phenolphthalein solution and titrate the sample with 0.5 N HCl until the pink color disappears. Reheat the sample to the boiling point, and if it turns pink, resume titration until the color once again disappears. Repeat this procedure until the pink color does not reappear on heating. Saponified waxes usually require two repetitions of heating and additional titration until the pink color does not reappear.

8. Calculation

8.1 Calculate the saponification number as follows:

$$\text{Saponification number} = \frac{(B - A)N \times 56.1}{C}$$

where:

A = millilitres of HCl solution required for titration of the sample,

B = millilitres of HCl solution required for titration of the blank,

C = grams of sample used, and

N = normality of the HCl solution.

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[1] This test method is under the jurisdiction of ASTM Committee D-21 on Polishes and is the direct responsibility of Subcommittee D21.02 on Raw Materials.
Current edition approved May 26, 1989. Published July 1989. Originally published as D 1387 – 55 T. Last previous edition D 1387 – 84.

[2] *Annual Book of ASTM Standards,* Vol 15.05.

9. Precision and Bias

9.1 Precision and bias have been established only for light-colored waxes melting below 100°C.

9.1.1 Duplicate results by the same operator shall not be considered suspect unless they differ by more than ± 1.3 saponification numbers (95 % confidence limits for average).

9.1.2 Results reported by two laboratories shall not be considered suspect unless they differ by more than ± 3.2 saponification numbers (95 % confidence limits for average).

9.2 Dark-colored waxes or wax melting above 100°C, or polyethylene copolymer waxes may exhibit poorer reproducibility when running saponification values. See Scope.

SCHÜMANN SASOL

Analytical Method No : 023-98
Revision No : 0
Date : Mar 1998
Effective from : Mar 1998
Page : 1 of 8
Copy No :

DETERMINATION OF THE ACID AND SAPONIFICATION VALUES OF ORGANIC SOLVENTS AND WAXY PRODUCTS, AND THE CALCULATION OF THE ESTER VALUE

1 REVISION

Method No	Date	The nature of Revision
023-98	March 1998	New method

2 SCOPE AND APPLICATION

2.1 This method is suitable for the determination of acid, saponification, and ester values in waxy products and xylene-soluble organic solvents in the range of 0,1 to 100 mg KOH/g for the acid and saponification values, and 0,2 to 100 mg KOH/g for the ester values.

2.2 Organic chlorides, nitriles and amides may be hydrolysed by the reagent and are a possible source of error. Ketones interfere slightly but aldehydes consume alkali and therefore interfere significantly if present in high concentrations.

3 SIGNIFICANCE

This method is applicable for quality control on specific organic solvents and waxy products concerning their total acid and ester content.

4 SUMMARY OF METHOD

4.1 The acid value is determined by the titration with 0,1M KOH solution.

$$RCOOH + KOH \rightarrow RCOOK + H_2O$$

4.2 The sample is refluxed with an excess volume of 0,1M Methyl Cellosolve / KOH solution. The excess KOH is determined by a titration with HCl, whereafter the saponification value is determined by the KOH consumed.

$$RCOOH + RCOOR + KOH\ (\text{excess}) \rightarrow RCOOK + ROH + KOH$$

4.3 The ester value is calculated by subtracting the acid value from the saponification value.

5 APPARATUS

5.1 Erlenmeyer flasks; 250 cm^3, wide mouth.

5.2 Burette; 20 cm^3, graduated in 0,02 cm^3 sub divisions, but a Mettler or Metrohm automatic titrator is more suitable.

5.3 Analytical balance; 300 g max, accurate to 0,01 g.

5.4 Pyrex flat bottom flask or equivalent; 250 cm^3, B29 sockets.

5.5 100 cm^3 Advanced Composite Vessel (ACV) fitted with 13,5 bar rupture membrane and carousel.

5.6 Double surface condenser; B29 cone, 20 cm length.

5.7 1 kW Microwave oven with modified switchgear.

5.8 Heating mantles; 250 cm^3.

5.9 Various pipettes.

5.10 Pro-pipette.

6 REAGENTS

6.1 Hydrochloric acid, 33-35 mass %.

6.2 Phenolphthalein indicator.

6.3 Potassium Hydroxide, 85% minimum, potassium carbonate 0,7 mass % maximum.

6.4 Reduced methyl cellosolve

6.5 Ethanol

6.6 Xylene or Solumix

6.7 Methyl cellosolve / KOH solution (0,1M)

Weigh 7 ± 0,1 g potassium hydroxide in a 100 cm^3 glass beaker. Rapidly rinse the pellets with a small volume of deionised water and then discard the water. Dissolve the remaining pellets in a small volume of deionised water and dilute to 1 dm^3 with reduced methyl cellosolve. Standardise according to Analytical Method no 2.0.2.

6.8 Phenolphthalein (or thymolphthalein) indicator

Dissolve 5 ± 0,1 g of phenolphthalein (or thymolphthalein) in 500 cm^3 methanol and dilute to 1 dm^3 with distilled water. Samples which exhibit a reddish colour, should be titrated with thymolphtalein.

6.9 Hydrochloric acid (0,3 M)

Dilute 27 ± 1 cm^3 of concentrated hydrochloric acid in a 1 dm^3 volumetric flask, containing approximately 500 cm^3 deionised water and dilute to the 1 dm^3 mark with deionised water. Standardise according to Analytical Method No. 2.0.3.

7 SAFETY PRECAUTIONS

7.1 Melted wax may cause severe burns. It should be handled with care. Use cotton gloves and wear a long sleeved shirt or laboratory coat to prevent part of the arms or hands to be exposed while handling hot waxes or organic solutions.

7.2 Xylene (and Solumix) fumes are poisonous. It irritates the eyes and respiratory system and induces dizziness. The fumes can be absorbed through the skin. Avoid inhaling and prevent contact with the skin or eyes. In case of eye contact, rinse thoroughly with distilled water and seek medical attention. In case of skin contact wash with soap and water. Xylene is highly flammable - keep away from open flames or any other ignition sources.

7.3 Concentrated hydrochloric acid is highly corrosive and causes burns. Always wear protective clothing when working with the acid. In case of contact, wash immediately with running water.

7.4 Handle all organic solvents as potentially hazardous.

8 PROCEDURE

8.1 Acid value

8.1.1 Weigh 1 to 20 g sample in case of waxes, or 1 to 40 g in case of organic solvents (note 11.1), exactly to the nearest 0,01 g, in a 250 cm^3 Erlenmyer flask.

8.1.2 Add 50 cm^3 xylene and heat slightly on a hot plate.

8.1.3 Carefully add 25 cm^3 ethanol and heat slightly on a hot plate. Titrate, while still hot, against 0,1 M Methyl cellosolve KOH solution with phenolphthalein indicator (Titration: V_1 cm^3).

8.1.4 Prepare a blank, following the same procedure with the exception of any sample (Titration: V_2 cm^3).

8.1.5 If $V_2 > 0,1$ cm^3, use xylene with a lower acidity.

8.2 Saponification value (Method A)

8.2.1 Weigh 1 to 20 g of the sample in case of waxes, or 1 to 40 g in case of organic solvents (note 11.1) exactly to the nearest 0,01 g, in a 250 cm^3 flat bottom flask.

8.2.2 Add 30 cm^3 0,1 M methyl cellosolve KOH solution and reflux for 45 minutes on a heating mantle.

8.2.3 Add 20 cm^3 xylene through the condenser and bring the solution back to boiling point.

8.2.4 Cool down slightly and remove the flask from the heating mantle and condenser.

8.2.5 Add phenolphthalein indicator and titrate with 0,3 M HCl solution using a magnetic stirrer till colourless (V_3). If the endpoint is obscured by dark coloured samples, switch off the magnetic stirrer and wait for the layers to separate. Continue the titration until the bottom layer is colourless.

8.2.6 Return the flask to the heating mantle and reflux again for 5 minutes. If the pink colour returns, cool it down slightly and titrate again till colourless (V_4).

8.2.7 The total titration $V_5 = (V_3 + V_4)$

8.2.8 Do a blank, following the same procedure without any sample. (Titration: V_6 cm^3).

8.3 Saponification value (Method B)

8.3.1 Weigh 1 to 20 g of the sample in case of waxes, or 1 to 10 g in case of organic solvents (note 11.1) exactly to the nearest 0,01g in 100 cm^3 Advanced Composite Vessel (ACV).

8.3.2 Add 30 cm^3 0,1 M methyl cellosolve KOH solution and heat in microwave oven for periods as shown in table 1.

8.3.3 Remove ACV's from the microwave oven and place in cold water for five minutes.

8.3.4 When cool enough to open, add phenolphthalein indicator and titrate with 0,3 M HCl solution until the solution is colourless (V_3).

8.3.5 Close the ACV and replace in the microwave oven for 5 ±1 minutes. If the pink colour returns, cool it down by placing the ACV in water and titrate again till colourless (V_4).

8.3.6 The total titration $V_5 = (V_3 + V_4)$

8.3.7 Do a blank, following the same procedure without any sample. (Titration: V_6 cm^3).

9 CALCULATIONS

9.1 Acid value, mg KOH/g $= \dfrac{(V_1 - V_2) \times M_1 \times 56.1}{m}$

9.2 Saponification value, mg KOH/g $= \dfrac{(V_6 - V_5) \times M_2 \times 56.1}{m}$

9.3 Ester value, mg KOH/g = (Saponification value) - (Acid value)

Where:
V_1 = Volume 0,1 M KOH used for sample, cm^3
V_2 = Volume 0,1 M KOH used for blank, cm^3
V_5 = Volume 0,3 M HCl used for sample, cm^3
V_6 = Volume 0,3 M HCl used for blank, cm^3
M_1 = Molarity of KOH
M_2 = Molarity of HCl
m = Mass of sample used, g
56,1 = Molecular mass of KOH

10 PRECISION

10.1 Acid value (95% repeatability)

Duplicate results obtained by the same analyst should be considered suspect if they differ by more than 4,0% at a level of 30 mg KOH/g.

10.2 Saponification value (95% repeatability)

Duplicate results obtained by the same analyst should be considered suspect if they differ by more than 5.0% at a level of 60 mg KOH/g.

11 NOTES

11.1 Enough sample must be used to ensure a titration difference between the sample and the blank of at least 0,2 cm^3. Use at least 12 g of the sample if the acid content is expected to be less than 0,1 mg KOH/g.

11.2 Solumix can be used instead of xylene as a solvent.

11.3 Rinse the reflux condensers with water and acetone, before and after usage.

11.4 Wash ACV's with warm water and use plastic brush to clean. Do not use metal brushes or scourers. Rinse with deionised water, do not use acetone.

11.4 Dark coloured samples, or samples with high acid and/or ester values, can be diluted with xylene or iso-propanol.

12 REFERENCE

12.1 ASTM D1386 - 83 (reapproved 1988)

12.2 ASTM D1387 - 89

12.3 Sasol Analytical Method No. 2.72/95

Table 1 Oven settings and times for saponification values

Number of Samples	Timer Setting	Heating Time
Two	B 004 S	9 ± 1 minutes
Four	B 004 S	15 ± 1 minutes
Six	B 004 S	24 ± 1 minutes

PREPARED BY: _____ _______________

APPROVED BY: _______________
(1) DIVISIONAL HEAD
SCHÜMANN SASOL LABORATORY SERVICES

____
(2) MANAGER, WAX RESEARCH

APPENDIX III: Abstract of Microwave Saponification Value Method Poster, presented at International Microwave Chemistry Conference, Prague, 6-11 September 1998.

SAPONIFICATION VALUES OF WAXES USING MICROWAVES INSTEAD OF CONVENTIONAL HEATING

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The determination of saponification value is a method used to determine the number of acid and ester groups in a substance. It is a particularly important parameter for users of oxidised waxes, both natural and synthetic, as ester functionality determines the utility of the wax as well as being a significant quality control test. The saponification number (or value) is defined as the number of milligrams of potassium hydroxide required to hydrolyse 1 g of the sample and is a measure of the amount of saponifiable matter present.

An ASTM method exists [1], which involves refluxing the wax for a substantial time (over 3 hours) with an excess of base (KOH) in ethanol. The excess KOH is determined by titration with HCl solution, whereafter the saponification value is determined by the KOH consumed:

$$\mathrm{RCOOH + RCOOR' + KOH\ (excess) \rightarrow RCOOK + R'OH + KOH}$$

If the acid value has been previously determined (as is usually the case), the ester value may be calculated by subtracting the acid value from the saponification value.

Recently we at Schümann-Sasol Research and Development [2] have been investigating the use of microwaves for various purposes and have subsequently developed a method for determining saponification values using microwave heating. We have reduced the total analysis time from more than 3 hours per sample to as little as 30 minutes for four samples (typically the number of samples our quality control laboratory desires to perform at any one time) by substituting microwave digestion for the conventional heating process, and using methyl cellosolve (2-methoxyethanol) instead of ethanol.

In the new method the wax (1 g) is accurately weighed into a Teflon sample digester (100 $\mathrm{cm^3}$) fitted with a rupture membrane system, commercially available from CEM Corporation [3]. Potassium hydroxide in methyl cellosolve (30 $\mathrm{cm^3}$ of 0.1 mol $\mathrm{dm^{-3}}$) is added to the vessel by burette and the vessel is closed. Three other vessels are similarly prepared (with wax or as blanks – a blank result is necessary for calculation of the saponification value). The vessels are evenly placed on a carousel (also available from CEM Corporation) and the carousel is place in the microwave oven.

We use a 1000 W domestic microwave oven [4], which has been modified based on work by Pougnet [5]. The modifications [6] entail replacing the control panel with new switchgear which allows the power to be controlled in square-wave fashion (i.e. full power for *x* seconds, no power for *x* seconds, alternating, with *x* being selectable). Experiment resulted in us using a periodicity of 4 seconds and a total time of 15 ± 1 minutes. The reason for the periodic application of power is to prevent the vessel from over-pressurising. At the end of this time the vessels are removed from the oven and placed in cold water for cooling. This takes about 5 minutes, when the vessels are sufficiently cool to be opened. If the lid of the vessel is still tight it should be cooled further to ensure that the pressure inside the vessel is the same as outside.

The solution is titrated in the vessel with aqueous 0.3 mol dm^{-3} HCl using phenolphthalein as indicator. As with the conventional method [1], the solution is titrated until near colourless. The vessels are then closed and placed back in the microwave oven for a further 5 ± 1 minutes. The vessels are removed from the oven, cooled again in water , opened, then the solution is titrated until colourless. Calculation of the saponification value is as for the conventional method [1].

Samples of two different oxidised wax products, Paraflint A1 (an oxidised wax with typical acid value of 27 mg KOH/g) and Paraflint A2 (a saponified wax with typical acid value of 12 mg KOH/g) [7] were analysed by both methods at least 20 times. We present results which show that the microwave method for the determination of saponification value gives the same results as using the conventional method, with repeatability and reproducibility at least the same as the ASTM method [1], though there is some evidence indicating that the microwave method has better repeatability.

The method is suitable for the determination of saponification values in waxy products in the range 0.1 to 100 mg KOH/g. Organic chlorides, nitriles and amides may be hydrolysed by the reagent and are possible sources of error. Ketones interfere only slightly but aldehydes consume alkali and therefore interfere significantly if present in high concentration. However, these interferences are unlikely to be found in natural or synthetic waxes.

[1] American Society for Testing and Materials, ASTM method D1387-89.

[2] Schümann-Sasol is a company formed in 1995 by merger of Sasol Waxes (the wax division of Sasol Ltd) and Hans-Otto Schümann GmbH, a petroleum wax company.

[3] CEM Advanced Composite Vessel, from CEM Corporation, P.O. Box 200, Matthews, NC 28106, USA.

[4] Sanyo model EM-V860, 1000 W.

[5] M.A.B. Pougnet: 'Design of Microwave Heating Equipment for Laboratory Applications', Ph.D. Thesis, University of Cape Town, 1993.

[6] Details are available from the authors. Several manufacturers offer suitable microwave equipment, but we found the modification route to be the most cost effective for our purposes.

[7] Paraflint is a registered tradename of Schümann-Sasol.