Optimization of rolling mill oils evaluation using FT-IR spectroscopy

By

Pheladi Junior Mogwaneng

Submitted in partial fulfilment of the requirements for the degree

Master of science

In

Chemistry

In the faculty of Natural & Agricultural Science
University of Pretoria
Pretoria
Republic of South Africa

April 2004

Acknowledgements

I would like to thank my advisor, Prof. D. De Waal for guidance through out this project, Prof J.C.A Boeyens for his inputs and fruitful discussions, my family for their encouragement and my colleagues for their willing support especially Dr Alan Bentley for editing the text and Mrs Elsie Snyman-Ferreira.

A special word of thanks to ISCOR Technology division for supplying us with rolling oils and IMMRI (Industrial Metals and Minerals Research Institute) for allowing us to use their instrument. Financial support from the University of Pretoria and the NRF, Pretoria, is gratefully acknowledged.

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Abstract

During the cold reduction of steel sheet in a rolling mill, rolling oils are used for lubrication to provide the desired steel surface. Rolling oil formulations consist largely of mineral oils, glycerides and/or synthetic esters, fatty acids, emulsifiers and additives. These oils are generally used as 2-5% emulsions and will be subjected to high temperature and pressure during use. This results in chemical changes within the oil that can affect steel surface cleanliness after annealing. It is advantageous to have rolling oils that are stable but easily removed during annealing and leaving a minimal amount of residues. Thus in the field of rolling mill technology the surface quality of rolled product and stability of rolling oils are critical in the selection of lubricants. Additionally, production cost and environmental impact are also critical in the selection of lubricants. In this study, the performance of vegetable-based rolling oils was investigated by recording the FTIR spectra of the oils using Horizontal Attenuated Total Reflectance, an internal reflection accessory, before and after systematic heat treatment. Evidence was found that the vegetable-based oils degraded on heating and the spectroscopic analysis indicated that this was due to rearrangement of unsaturated components from a cis to a trans configuration.

Samevatting

Gedurende die koue verwerking van staal in ‘n walsmeule word walsolies gebruik om smering te verskaf ten einde die verlangde staaloppervlak te verseker. Walsolies bestaan grootliks uit mineraalolies, gliseriedes en/of sintetiese esters, vetsure, emulsifiseerders en byvoegings. Hierdie olies word normaalweg gebruik as 2-5% emulsies en word aan hoë temperatuur en druk tydens gebruik blootgestel. Dit lei tot chemiese veranderinge in die olie wat die staal se suiwerheid na uitgloeiing kan beïnvloed. Dit is voordelig om walsolies te gebruik wat stabiel, maar steeds maklik verwyderbaar tydens uitgeloeiing is, en min residu agterlaat. In die veld van walstegnologie is die oppervlakkwaliteit van die gewalsde produk en die stabiliteit van die walsolies dus van kritiese belang in die keuse van geskikte smeermiddels. Produksiekoste en omgewingsimpak speel ook ‘n belangrike rol. Tydens hierdie ondersoek is die gedrag van plantaardige walsolies bestudeer deur die *FTIR* spektra van die olies met behulp van *Horizontal Attenuated Total Reflectance, ‘n interne refleksie bykomstigheid*, voor en na sistematiese hittebehandeling te meet. Die resultate dui daarop dat plantaardige olies tydens verhitting degradeer en spektroskopiese analiese toon aan dat hierdie degradasie te wyte is aan die herrangskikking van onversadigde komponente van ‘n cis- na ‘n transkonfigurasie.

- Chapter 1 -

An introduction to the problem

CHAPTER 1.

1.1. Introduction to cold rolling lubrication

Cold rolling operations associated with the flat processing of steel products involve the use of rolling lubricants. These materials, usually in the form of fatty or mineral oils, applied either neat or in emulsion form, greatly facilitate the reduction of the strip in that they considerably reduce the rolling force required for deformation. By so doing, they also (a) make the attainment of acceptable "shape" or flatness in the rolled product much easier, (b) lessen roll wear, (c) reduce roll and strip temperature, and (d) prevent rusting of the reduced strip.

Without knowledge of the effectiveness of the rolling lubricants used, the satisfactory operation of commercial rolling facilities becomes more difficult to achieve. From an economic viewpoint, it is desirable to use the cheapest material that will provide adequate lubrication in the roll bite. Generally speaking, lubricant consumption ranges from 3 to 8 lbs. per ton of steel rolled. From a practical viewpoint, reduction in the quantity of rolling lubricant used is not always feasible because of the "drag out" of the lubricant on the surface of the rolled strip, due to the skimming of the lubricant tanks and because of the other operations necessary to maintain the aqueous dispersion of the lubricant in a satisfactorily clean condition. Accordingly, it is often easier to achieve economies by changing the nature of the rolling lubricant rather than by reducing its consumption.[1]

Although cold rolling lubricants have been extensively used since the early 1930's, research into their behaviour was not undertaken to any significant extent until the late 1940's. Even then, for a variety of reasons, the research data was often difficult to interpret or relate to other rolling specifications. Moreover, because of incorrect assumptions relating to rolling models, computed values of the coefficient of friction on the roll bite were often of questionable accuracy.

The characteristics of an ideal rolling lubricant.

The desirable characteristics of a rolling lubricant may be listed as follows: [2, 3, 4]

1. It must provide a lubrication and a corresponding rolling force so that satisfactory strip shape is obtained.
2. It should be easy to apply, either neat or in the form of an emulsion.
3. It should not make mill “housecleaning” more difficult by excessive “plating out” on the mill.
4. It should not seriously impede the heat transfer from the rolls and strip to the coolant.
5. It should be consistent in performance until it decomposes.
6. It should provide the desired degree of protection from rust in the rolled product.
7. It should be easily removed from the strip after rolling.
8. It should be non-toxic and not cause dermatitis or other health problems on contact.
9. It should be economical with respect to usage.

With time, another characteristic was added to steel industry cold rolling oils. It required that the cold rolling oil had to be recoverable after use. This brought about the requirement that the cold rolling oil should be oxidatively stable with regard to high temperature and water. The oil was not only used to protect the steel from friction and corrosion, it was also used to measure the steel cleanliness. The steel cleanliness was measured with a Tape test. This test is only done after the steel has been put through the mill. Any detrimental condition of the oil was seen after the process. This caused a very high cost for the industry because the steel cleanliness could only be measured after the process and no modification can be made to the oil. Therefore, it is considered important by the steel industry to have a parameter of predicting the steel cleanliness with regard to the neat oil. The Tape test is shown in Figure **1.1** and an 80% reflection shows a good lubricant.

Tape test to measure steel cleanliness

(a)

(b)

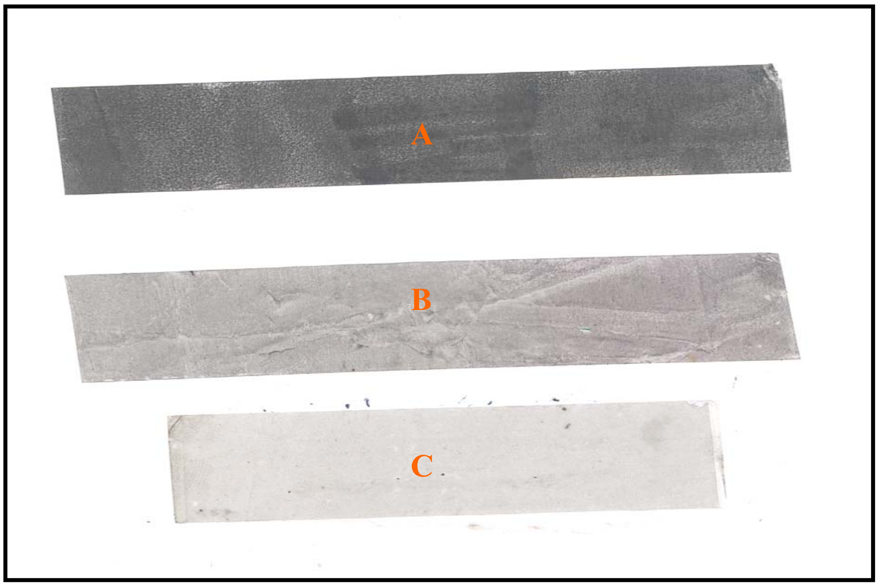


Figure 1.1: The reflectance measurement of the steel in (a) is shown in (b) where A gave a 21.7%, B gave 38.3% and C gave 62.6% reflectance.

The use of cold rolling oils on rolling mills, the expectations and specifications set for this usage and the problems encountered, initiated research over a wide front in materials research and included a number of specialized areas. Numerous publications exist, dealing with: the rolling oil itself, application procedures, different test procedures, different composition of rolling oils, oxidation mechanism of the oils etc [5, 6, 7].

1.2. Dissertation subject

This dissertation explores the reasons for the huge variations experienced in the cold rolling properties of synthetic oil, tallow oil and vegetable oil. The oil oxidation results, obtained with specific test procedures, were interpreted with the aid of analytical techniques.

Products, which originated from different cold rolling suppliers for the cold rolling process, were tested. The synthetic based cold rolling oil gave good oxidation stability, while the vegetable based oil gave poor oxidation stability. These circumstances necessitated the testing of the major components of the vegetable based oil. The site related conditions in producing the steel strip and the specific oil used, required the investigation of the total problem to determine the mechanism(s) responsible for poor oxidation stability of the oil.

1.3. Overview of the previous rolling oils research

It was obvious that the specific set of conditions valid in this case, was unique in more than one aspect regarding the production processes and the cold rolling requirements. The aim of the literature overview was to extract the relevant information that could assist this study.

1.3.1. Introduction

It can be understood that poor steel cleanliness problems experienced with the application of lubricants, have plagued the industry and industrial scientists since oils were used as lubricants during sheet and tinplate production. As far back as 1958, Werner Lueg and Paul Funke[8] published work done on rolling oils concerning rolling tests with commercial rolling oils under different conditions of operation adapted to practice. The number of rolling oil compositions is numerous, as is the number of methods used to evaluate these rolling oils. Evaluation of the steel surface cleanliness problem, however, indicates that the following variables have the predominant influence on any rolling oil formulations, namely:

(a) Properties of the environment in which the rolling oil is tested or has to function,
(b) Properties of the rolling oil itself,
(c) Properties of the steel itself.

Although all properties remain relevant to the steel surface cleanliness problem as a whole, only property (b) is addressed in this study. The important influence of the rolling oil properties to steel surface cleanliness has been realized since late 1974 by Walz.[9] It was not until 1983 that Keiichi Tanikawa and Yuji Fujioka [10] reported on organic carbon stains on a cold rolled sheet surface. They focused on how the lubricating oil residue on steel sheet surface behaves through thermal decomposition during the annealing process. It was also discovered that the cold rolling lubricating oil left on the surface of “as cold rolled steel sheet” remains as decomposed residue, though in trace amounts, and that this residue primarily consists of fatty acids and esters. Although this result could have been due to oxidation, it put a question mark behind the possible influence of the bulk composition of the rolling oil properties. In 1992 de Werbier [11] and his co-workers also indicated the importance of the relationship between chemical composition of rolling lubricants and organic surface residues. They simulated the interaction of steel surfaces with various compounds contained in rolling lubricants. They showed with Fourier-transform infrared spectroscopy (FTIR) that certain compounds engage in chemical reactions with the surface as a function of temperature. The determination of the oil residues on the steel surface only became a possibility with the instrumentation of the spectroscopy analysis technique towards the beginning of the nineties. [12] The analytical techniques like Nuclear magnetic resonance (NMR), Gas Chromatography (GC), Mass Spectrometry (MS), Infrared Spectroscopy (IR), Thermo gravitational analysis (TGA), High-pressure liquid chromatography Infrared (HPLC-IR) et cetera, remained at a lower standard of development in the steel plant laboratories. As is normal with all new techniques, it needed a growth period for the techniques to become established and for the user to gain experience. From 1983 onwards, steel surface cleanliness related analytical results started to appear in the literature. As stated by Broekhof, [13] a considerable amount of effort is being spent worldwide to look at ways to increase productivity, lower overall cost and improve product quality were lubricants are important in reaching these goals.

The main drive to investigate the poor steel cleanliness phenomenon was initiated by the cold rolling mills supplying coating lines and the automotive industry. Therefore, the initial steel cleanliness problem concerns the rolling oil composition. The most used quality analysis of the rolling oils during the early 1980’s was by measuring the pH, acid value, saponification value, oil content, etc. These indicative methods only give the total change in the amounts of acids and esters contained in the oil. This type of system specific research, limits the use and implementation of the results obtained. Due to the unique demands from each cold rolling mill product, oils are formulated and manufactured according to the type of mill and method of application, resulting in a large range of different products with compositions unknown to the steel industry.

1.3.2. The oil/surface interaction

Numerous factors from various processes, hot mill, pickling line and annealing practices all impact on steel surface cleanliness. The properties of the organic residues on the steel surface are important in interpreting the steel surface cleanliness results. The lubricant, usually applied as an emulsion, should form an adequate film in the inlet of the roll bite. This forming of a film on the steel surface is mainly governed by emulsion properties such as plate-out (homogeneous covering of the steel surface with a thin layer of an oil). Plate-out at a given concentration and temperature determines how much oil is delivered to the strip from the emulsion. Tanikawa and his co-worker's [10] attention was focused on organic carbon, one of the surface residues that adversely affected the surface cleanliness of cold rolled steel sheet, and the property alteration behaviour of the rolling oil adherent to the steel in the as rolled condition during annealing was analysed by analytical techniques. Many reports were published that analysed inorganic carbon deposited on the sheets by such techniques as Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), [14] but organic carbon was not discussed in depth.

In the work by Smallheer [15] and Wills, [16] they focused on lubricated tribological systems, operating under conditions of high load and low speed, that frequently run in the boundary lubrication regime. They continued stating that the chemistry occurring within the few nanometres of the surface becomes a critical determining factor with respect to properties such as frictional forces and wear. In order to control the chemistry in this important interfacial region, lubricants manufacturers blend additives into oils. Cameron [17] and Studt [18] added that these additives either adsorb onto the sliding surface upon contact or react with the surface under extreme conditions, and in both cases form protective layers, which protect the underlying solid surfaces, see Figure **1.2.**

In the work done by Christopher McFadden [19] and his co-workers, they have endeavoured to summarize the selected significant results where surface science is contributing to the knowledge of the chemistry of boundary lubrication. P. de Werbier and his co-workers [11] studied the relationship between chemical composition of the rolling lubricants and organic surface residues. Most of their investigation conducted in this field relate to the recovery of organic compounds on the surface with the aid of an organic solvent. By using this approach, they were able to show that the compositions of a surface film can differ considerably from that of the base oil. Tusset and Muller[12] were also able to show, from the tested rolling mill and lubricant, degradation of part of the esters and a corresponding increase in di-glycerides as well as the absence of emulsifiers in the surface film after rolling.

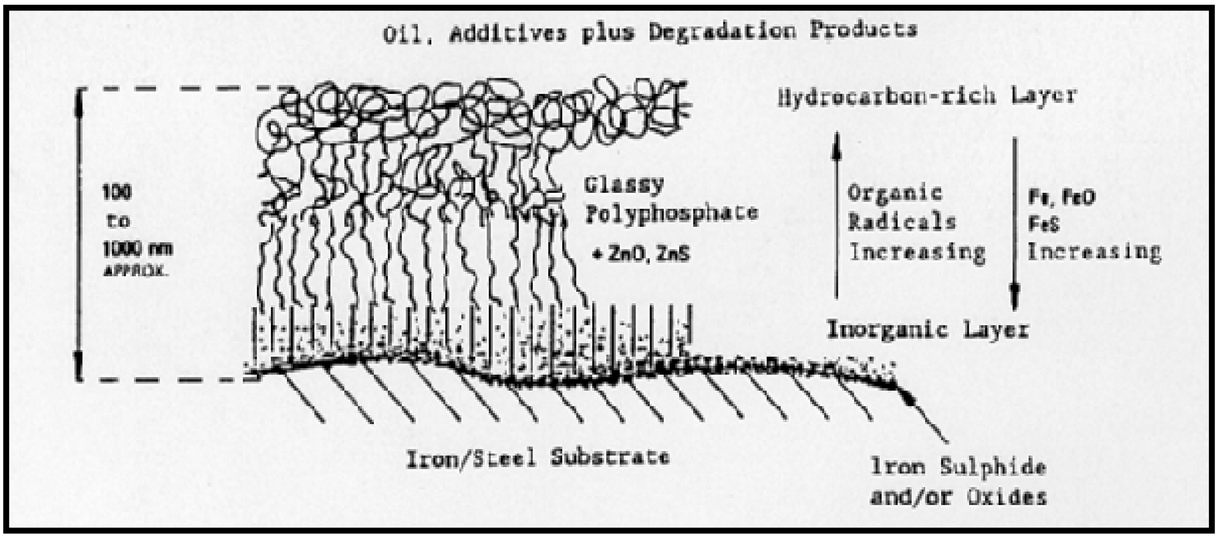


Figure 1.2: Schematic layer of residues left after cold rolling showing oil, degradation products, iron fines, additives etc. [20, 21]

P. de Werbier and his co-workers [11] approached this matter for the second time simulating the organic compound/metal interaction with the aid of model molecules. Their results showed the strong interaction of the fatty acids and the metal surface. They therefore decided to study films composed of saturated fatty acids (stearic acid) or unsaturated fatty acids (oleic acid). Their simulations assist in understanding the mechanisms of formation of surface residues, which enable the molecules responsible for these reactions to be identified. They were not able to identify the features of these molecules in the neat rolling oils and correlate them to surface cleanliness.

There are numerous methods for identifying thin surface layers (Auger, ESCA, SIMS etc.) but, in the case of lubrication where one is interested in both the oil film and its interaction with the metal, these methods are not suitable. According to de Werbier and his co-workers, [11] two other techniques for characterizing surface, namely, Fourier-transform infrared spectroscopy (FTIR) and a combination of Mass Spectrometry and Thermodesorption could be used. The progress made by use of Fourier-transform spectroscopy in respect of sensitivity and rapidity was quite remarkable. Using this technique, it was possible to study the composition of the surface oil film.

The mechanism by which the oil oxidizes is by a free radical that leads to the formation of peroxy and epoxy intermediates, which eventually produce a variety of oxidation products, such as free fatty acids, aldehydes and ketones. The main reaction centre for the formation of these oxidized compounds is the carbon-carbon double bond.[22] However, advances have been made and everyone agrees that the most important factor pertaining to cold rolling oils is the amount of extraneous materials left on the steel surface after annealing and the most critical problem still remains the oxidation stability of the cold rolling oils.

1.3.3. Steel rolling process

The methods of steel manufacture differ essentially in the way the hot rolling; cold rolling and annealing treatments are used to obtain the required gauge and physical properties in the finished product.

Steel is usually produced by the following typical procedures [23].

(a) Hot rolling

Hot rolling is carried out by the hot-pack or the continuous strip process, yield either: (a) sheets rolled down to nearly the finished gauge and requiring only the further reduction that normally obtained by a cold rolling pass; or (b) continuous strip probably averaging from one-tenth to one-sixteenth of an inch in thickness and requiring heavy cold reduction to bring it to the designed finished gauge.

(b) Pickling

Pickling is the removal of the oxide scale or film by chemical treatment, generally in acid solutions. The steel sheet becomes coated with oxide at two distinct stages of the process, and two pickling operations are necessary. The first pickling operation is performed after hot rolling and its purpose is to remove the relatively thick oxide scale acquired after the reheat and rolling operations. The second pickling removes the thin oxide film, which forms on the sheets in the annealing operation, which follows cold rolling.

(c) Cold rolling

Cold rolling is performed by unwinding the hot rolled coil and passing the strip through pairs of horizontal rolls or mill "stands". Each roll set reduces the steel by a preset percentage until the finished thickness is reached.

The main purposes of cold rolling are:

1. *To reduce thickness or increase length or width of the sheets or strip.* Cold-rolling operations aimed at a significant amount of gauge reduction are usually described by the more specific term cold reduction, the application of cold reduction to steel practice

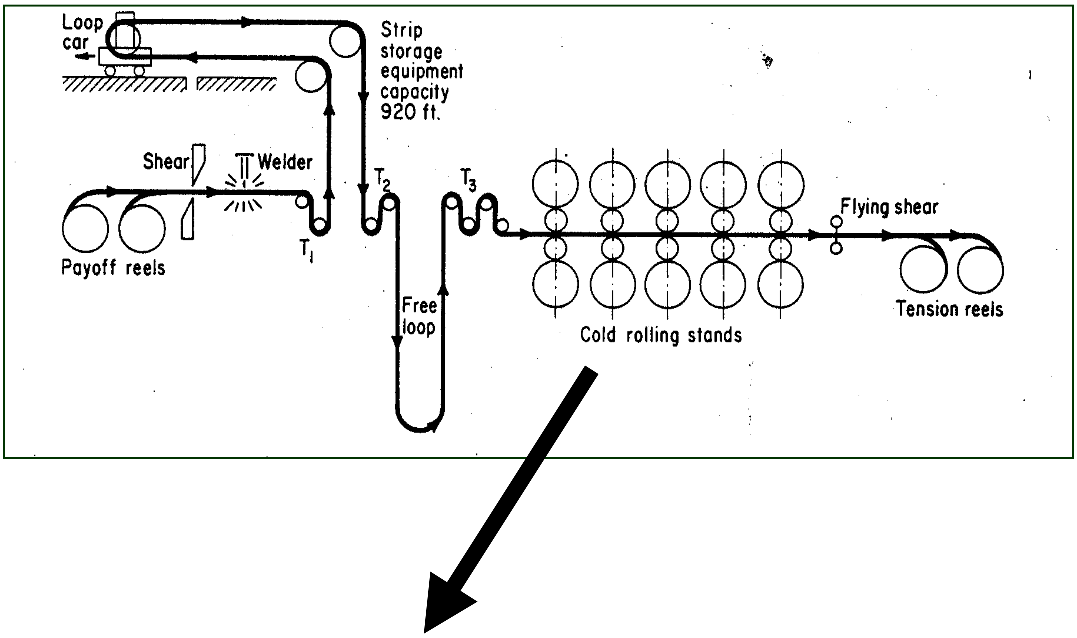
constitutes a well-known advance in technique. The process usually involves total cold reduction of about 60% or more and is carried out on mills either of the single-stand reversing type or continuous multi-stand tandem type.

2. *To improve the surface characteristics, chiefly smoothness, of hot rolled material.* Correctly controlled cold rolling always improves the smoothness and compactness of the surface of the stock.
3. *To flatten the stock.* Final cold rolling usually follows annealing. Annealed material may have a slight bow, corners of sheet may be bend in opening, or if stickers have been encountered the sheets may be crumpled. The cold-rolling operation serves to remove such physical defects and produce smooth, flat material. This process involves very small reduction (≈ 1%), and is known as temper rolling.
4. *To improve hardness or to modify other physical properties*. For some applications material of definitely increased mechanical properties, stiff stock, is required. This can be secured by cold rolling after anneal.

The industrial nature of steel surface cleanliness and the fact that the lubricants are used on industrial production lines under industrial conditions, necessitate the explanation of these lines. The schematic diagram of a five-stand Cold Mill is shown below in Figure **1.3**.

(c) Annealing

In most steel mills, two cleaning and annealing routes can be utilized to obtain the required surface specifications [24, 25]. These routes are the called Batch Annealing (BA-line) and the Continuous Annealing (CA- line). Although the aim of these two lines is the same, the processes used on the lines and the effectiveness of these processes, differ considerably.



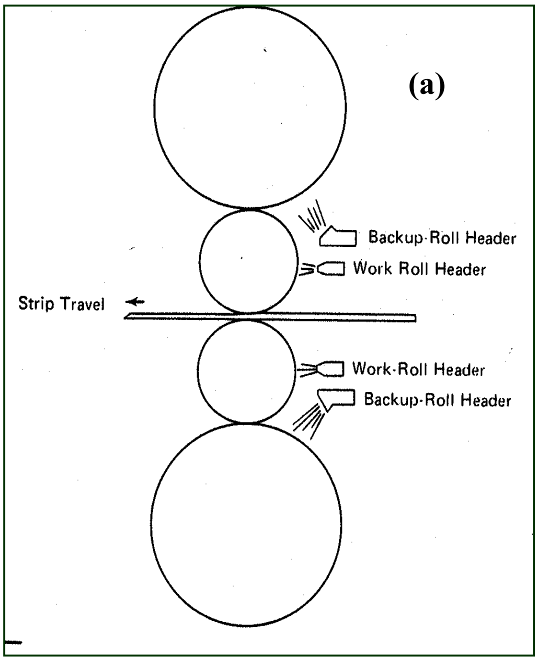


Figure 1.3: A schematic diagram of a five-stand cold rolling mill. The most important feature of the cold rolling line layout in this study is the location of rolling solution sprays on the mill stand [1].

These lines usually incorporate an alkaline electrolytic cleaning section. The cleaning section consist of the electrolytic cleaning process, followed by the necessary rinsing and surface drying stages before the steel strip enters the annealing section.

Annealing plants are design to satisfy two main criteria. Firstly, the control of the heating soaking and cooling cycles so as to obtain material of the required physical characteristics and grain structure. Secondly, control of the furnace atmosphere so as to minimize undesired surface effects such as oxidation, discoloration and staining from the oil residues left after cold rolling.

- Chapter 2 -

Cold rolling oils and the analytical technique

CHAPTER 2.

2.1. Introduction

The objective with the choice of experimental material, the experiment devised and the analytical technique used, was to determine the influence on steel surface cleanliness of the cold rolled steel with regard to the oxidation stability of the cold rolling oils.

The literature survey in chapter 1, stated that formulation of rolling oils is in the hands of long established suppliers, where they formulate and manufacture the oils according to the type of mill and method of application. The large number of lubricant combinations possible, the number of possible environments and the absence of standardized neat oil evaluation tests for steel surface cleanliness predictions, all add to the uncertainties regarding the use of lubricants on steel surfaces. As will be shown later, the evidence indicates that the poor steel surface cleanliness experience in the cases covered in this dissertation is related to the unsaturated rolling oils. Owing to this fact, an analytical technique was intensively applied and certain aspects of this technique are discussed.

2.2. Commonly used Cold rolling oils

Although rolling lubricants are sold commercially under brand names, basically their constituents are selected from oils, fats and waxes. Prior to World War II, palm oil was the most widely used rolling lubricant but the shortage of the imported lubricant spurred the search for substitute materials. This search led to the use of tallow and a large number of other organic materials presently in use today, many of which are blended with other materials such as emulsifiers, defoamers, antioxidants, and rust inhibitors. These additives, particularly emulsifiers, if used in excessive amounts, could diminish the effectiveness of the rolling lubricant in that it is not so readily plated-out on the rolls and strip from the rolling solution.[1]

Generally speaking, substitutes of palm oil (derived from vegetables and animal oils), for use as cold reduction lubricants, are esters of the trihydric alcohols, glycerol, with such saturated fatty acids as lauric, myristic, palmitic and stearic. These esters are called glycerides. In addition, esters of unsaturated acids of the acrylic series, such as oleic acid, are usually present in the vegetable oils.

When a fat contains a relatively large proportion of palmitic or stearic acid, it is solid and comparatively hard, like tallow, at ordinary temperatures. But, when it contains a relatively large proportion of oleic acid, it is soft and pasty, or liquid.

However, only vegetable oil is used in this study, because the poor oxidation stability problem that initiated this investigation occurred after the use of vegetable oils. During the cold rolling process, a high temperature of ≈ 400˚C is established, as rolling procedure involves continuous forward and backward extrusion of metal, which generates friction between the rolling surface and the strip. Before the usage of cold rolling oil the steel is covered with rust preventative oil. This oil layer serves two purposes, namely:

(a) Protecting the active, pickled surface from rust formation and,

(b) Serving as a lubricant during the first stage of the cold reduction process.

Due to the mechanical nature of the cold rolling process, and the fact that the friction can cause the temperature to increase up to ≈ 400˚C, a certain amount of oil left on the steel is oxidized. The high demands made on the surface of cold rolled sheet steel in a very competitive steel market, resulted in such stringent requirements for the lubricants that only minimum carbonaceous product and oil residues can be tolerated on the surface of material after being cold rolled. Most of this lubricant is removed from the surface by a detergent rinse during the last stage of the cold rolling process. Following a blow-drying step the cold rolled steel is coiled. The use of rolling lubricants and the surface detergents during cold rolling process, as well as the mechanical properties of the strip due to cold working, necessitates the cleaning, annealing and temper-rolling of the coils to produce a workable material that can be converted into sheet steel products with the required mechanical and surface properties.

2.2.1. Composition of rolling oils

Rolling oils consist of two major components; namely base oil and esters, as well as numerous additives.

- Base oil – mixture of paraffinic, naphthenic and aromatic hydrocarbons.
- Esters – compound components, may contain both;
  - (a) Natural (animal or vegetable) fat.
  - (b) Synthetic esters (esters of multifunctional alcohols such as trimethylolpropane, neopentyl glycol, pentaerythritol etc. with a variety of aliphatic chains or branched chain acids.

Acids incorporated in both types of esters may also vary with the degree of unsaturation. According to N. Croall, [26] a typical composition of fatty acids present in rolling oils as esters is;

(a) Oleic acid – 47.2%
(c) Linoleic acid – 24.4%
(d) Palmitic acid – 15.0%
(e) Stearic acid – 9.6%
(f) Lauric acid – 1.6%
(g) Myristic acid – 0.7%

- Additives – kinds of additives are closely related to the oil performance, therefore the following classes of additives may be distinguished in Table **I**;

Table I

Typical additives used in cold rolling oils[27]

Kinds of additives	**Typical compounds**
Dispersants and detergents	Succinimides, neutral metallic sulphonates, polymeric detergents, phosphonates, amines.
Antiwear and extreme pressure agents	Zinc dialkyldithiophosphate; tricresylphosphates; organic phosphates, chlorine and sulfur compounds
Corrosion inhibitors and antioxidants	Organically active sulfur, phosphorus, nitrogen compounds such as phosphates, metal salt of thiophosphoric acid, Sulphurized waxes, terpenes; zinc dialkyldithiophosphate, aromatic amines, Sulphurized products, hindered phenols.
Viscosity index improvers	Polyisobutylene, methacrylate polymers, olefin copolymers- may incorporate dispersants.

2.2.2. Plant oils

Plant-based lubricants are much more biodegradable. For plant-based lubricants, oxidative stability and low temperature problems (solidification) are considered the most critical. Plant oils are highly unsaturated, biodegradable and have a high ester concentration. [28]

2.2.3. Mineral oils

Mineral oils are complex mixtures of hydrocarbons, which can be classified into three main chemical families according to their structure, i.e., paraffins, naphthenic (cycloparaffins) and aromatic. These chemical classes of hydrocarbons are known to differ in their biodegradability. Biodegradability rates of paraffins are higher than those of naphthenic hydrocarbons. Mineral oils have medium to low ester concentration and are saturated.

2.2.4. Synthetic esters

The synthetic fatty acids esters are increasingly employed in lubricants. Synthetic esters based on e.g. trimethylolpropane (TMP). neopentylglycol (NPG) and pentaerythritol have been developed for better surface cleanliness. Synthetic oils are saturated and have a very high concentration of esters.

2.2.5. Tallow oil

Natural animal fats are made up of triglycerides, which are esters of glycerol and fatty acids. The hardness or the softness of fat is in direct relationship to the fatty acids profile of the lipid. The more saturated the fatty acids, the harder the fat; the more unsaturated, the softer. Tallow based oil is the mixture of saturated and unsaturated fatty acids. It has free fatty acids, which polymerizes more easily than bonded fatty acids. [1]

2.3. Standard cold rolling oils control tests

(a) Criteria for evaluation of Lubricants

Rolling oil must exhibit a number of qualities that facilitate the rolling and subsequent processing of the strip, and it is desirable to evaluate a lubricant on the basis of all pertinent properties. Otherwise, situations may arise, for example, where a lubricant, used on the basis of the excellent lubrication it provides in the roll bite, cannot retain its lubrication for long periods as an emulsion or cannot be easily removed from the strip after rolling. In assessing the merits of a lubricant, the following criteria should be established:

(1) the lubrication it provides in the roll bite,

(2) how its lubrication is affected by physical conditions associated with the rolling operations.

(3) the stability of an aqueous emulsion of the oil and the factors that affect it,

(4) its cleanability and burn off characteristics, and

(5) the extent to which it affords rust or corrosion protection.

Although lubricants may be evaluated on full size production mills, it is not always desirable, for reasons of economy, to utilize a mill trial of a lubricant that may have little chance of being successfully used on a production basis. Basically, the logical purpose of lubrication tests is to be able to predict exactly how the lubricant will perform under specified circumstances on a production mill and the behavior of the residual oil film in subsequent processing operations.

(b) Present cold rolling control tests and problems.

At present, the items listed in Table II control cold rolling oils. As evident from the description of these items, the present control method regards the rolling oil as a single substance and investigates its changes. For instance, the saponification value depends on the molecular weight of the fatty acids, which constitutes fats and oil; and contaminants, which exist in the fats and oils and is essentially used for the quality control of fats and oils. The saponification value is used for the control of rolling oils because it expresses the amount of carbonyl groups (including carboxyl groups) per unit weight or gram, substances that contain carbonyl groups, such as animal and vegetable oils, are known to contribute to improvement in lubrication, and the amount of carbonyl groups is a measure of lubricating performance.

Table II

Rolling oil tests

Test	Description
Oil concentration	Oil concentration in water emulsion
Saponification value	Amount of -COO- groups (including -COOH) per unit weight of rolling oil(according to ASTM D94)
Acid value	Amount of -COOH groups per unit mass of rolling Oil (according to ASTM D974)
Residual carbon	Contamination control of rolling oil (index of strip cleanliness)
ESI	Emulsion stability index
SI	Spreading index
BOI	Burn-off index
pH	pH of emulsion
Viscosity	Viscosity of undiluted oil (according to ASTM D445, 40°C)
Density	According to ASTM D1217, 40°C
Falex test	Failure load [p.s.i. At 40°C]
Chloride test	According to ASTM D1317
Sulphur test	According to ASTM D1552
Flash point	According to ASTM D93

ASTM: American Society for Testing and Materials

When the rolling oil contains two or more compounds that have different saponification values, however, it is not appropriate to evaluate the lubrication of the oil by the saponification value. Rolling oils in general use now contain several compounds having saponification values and even if the overall saponification value of the oil is measured, the changes in each component cannot be known from the measurement. This is also true for the acid value.

2.4. Introduction to analytical technique

Chemical analytical techniques are used worldwide in the study of rolling oils problems[12]. The technique used in this project was Fourier Transform Infrared Spectroscopy (FTIR) using a Horizontal Attenuated Total Reflectance accessory. Due to the chemical sensitivity of this technique, extreme care was exercised throughout this study to avoid accidental contamination of the oils received from the steel mill. Oil and fats begin to decompose from the moment they are isolated from their natural environment. Atmospheric oxidation is the most important cause of deterioration in fats. This oxidative rancidity is accelerated by exposure to heat, light, humidity and the presence of trace transition metals [29]. Because acceptable rolling oil characteristics can be obtained on rolling oil standards, the variable results obtained only regards the rolling oils as a single substance and investigates its changes. It is in this domain that the chemical analytical techniques excel.

2.4.1. Fourier Transform Infrared Spectroscopy

Most of the analysis in this study was carried out on this apparatus, because of its chemical sensitivity.

Infrared radiation lies in the Electromagnetic Spectrum between the visible region and the microwave region. It is measured in units of frequency, wavenumber or wavelength, which are interrelated by the following equations: -

$$\mathbf{F\lambda = c}$$

(**F** is frequency in Hz., cycle/second or its multiples)

(**c** is the velocity of light in a vacuum)

$$\mathbf{v = 1/\lambda}$$

$$\mathbf{f = cv}$$

(**v** is the wavelength, **f** is the wavenumber)

The infrared is divided into three regions: Near, Mid and Far. Interest in the NIR has grown in recent years, particularly for process control, raw materials and finished product analysis, especially in the food and feedstuffs industries, where it is routinely used for qualitative analysis [30]. The Far infrared is principally concerned with rotational spectra, and crystal lattice vibrations. The Mid infrared is by far the most widely used region as it is involved with molecular vibrations typically found in organic molecules. It provides a wealth of structural information, as well as quantitative data.

When infrared radiation is directed on a sample it is either transmitted or absorbed by the sample or reflected from it. The total incident radiation is $\mathbf{I_0}$. On placing the detector behind the sample a measurement of radiation occurs. This is the transmitted radiation **I**. The detector does not normally measure the reflected/scattered radiation **S**.

$$\mathbf{T = I/ I_0}$$

$$\mathbf{\%T = 100I/ I_0}$$

$$\mathbf{Absorbance = Log\ (1/T)}$$

$$\mathbf{Absorbance = Log\ (100/\%T)}$$

The Fourier transform infrared spectrometer measures a background Interferogram (to give $\mathbf{I_0}$), then a sample Interferogram (to give **I**) and from this data calculates the percentage transmission of the sample. The total incident radiation is described by this formula:

$$\mathbf{I_0 = I_R + I_A + I_S + I_T}$$

Where;

- I_R = Reflected beam
- I_A = Absorbed beam
- I_S = Scattered beam
- I_T = Transmitted beam

The infrared light beams are schematically shown below.

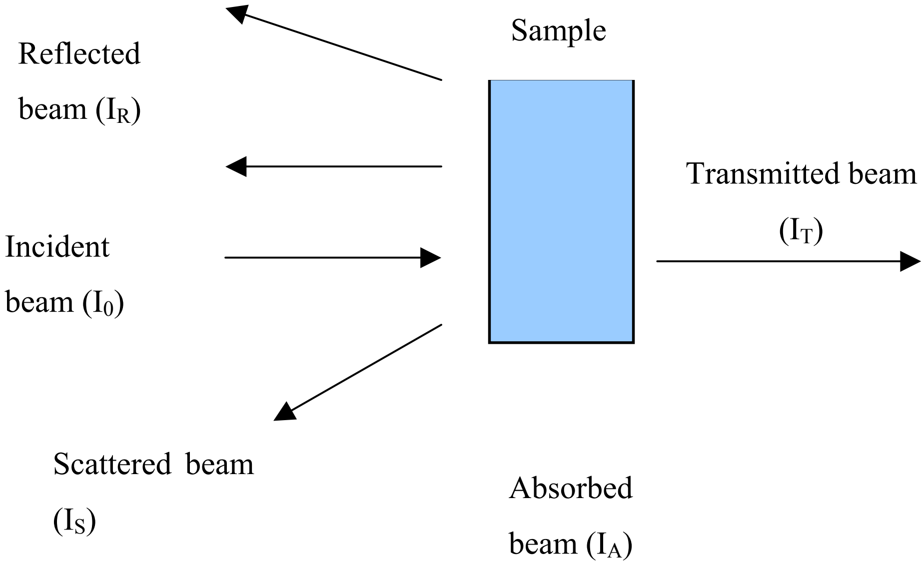


Figure 2.1: Schematic representation of the infrared light beams.

2.4.2. The Fourier Transform Process

The Fourier Transform Process is a mathematical formula, which is used to convert wave information. It is used in many areas of work, not only infrared spectroscopy (e.g. x-ray diffraction patterns) [31]. It has been applied to infrared spectroscopy for many years, and is now a standard technique. Virtually all-infrared spectrometers that are commercially available use the Fourier Transform process. In the case of Perkin-Elmer infrared spectrometer (which we are currently using) an Interferogram of the instrument background is measured and transformed to give a single beam energy spectrum, then the Interferogram of the sample is measured and transformed. This is then ratioed with the background spectrum to give a recognizable transmittance spectrum as the data shown on the spectrometer screen or hard copy device. The schematic FT-instrumentation is shown below where:

- The *Source* generates light across the spectrum of interest
- *Beamsplitter* sends the light into two directions at right angles.
- The *sample* absorbs all the different wavelengths characteristic of its spectrum
- The *detector* collects the radiation that passes through the sample and
- An electrical signal is put out and send directly to the *computer*.

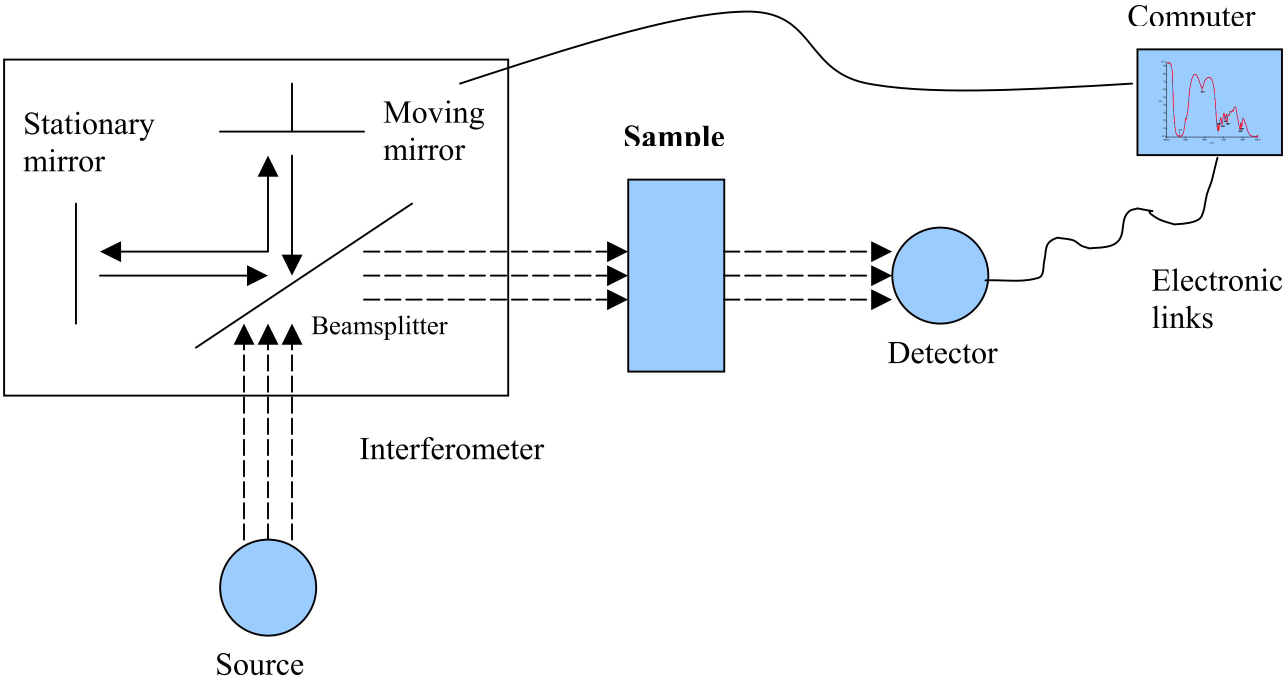


Figure 2.2: Schematic representation of typical Fourier Transform Spectrometer

2.4.3. Interpretation of the FTIR spectra

As a result of the crucial nature of the interpretations made from especially the FTIR spectra, a brief discussion is deemed necessary to assist and explain certain aspects of this interpretation.

One task of the spectroscopists is to obtain information about the molecular structure of an unknown molecule, by deducing how the observed absorption bands in the spectrum relate to the possible vibrational modes of the molecule. The theory of infrared spectroscopy essentially relates to simplified mass models, which can be used to represent the structure of natural molecules whose vibrational behaviour can be described by the classical principles such as:

(a) Activity
(b) The 3N-6 (non-linear) and 3N-5 (linear) Rule
(c) Diatomic Molecules
(d) Tri-atomic Molecules
(e) Tetra-atomic Molecules (XY_3)
(f) Penta-atomic Molecules (XY_4)
(g) Multiatomic Molecules

A variety of features can be seen in a typical infrared spectrum such as:

(a) Fundamental (group) vibrations
(b) Overtones
(c) Combination bands
(d) Skeleton vibrations (fingerprint region)

As long ago as 1882 Abeney and Festing noted that among the spectra they measured, those known to contain a hydroxyl group all absorbed near 3µm (3300 cm^{-1}) [32]. This is now recognized as the first characteristics group frequency. The converse of the statement may not be true i.e. compounds absorbing at 3µm may not necessarily contain an OH group (in fact N-H groups absorb in the same region), and further experimental evidence was obtained to find out the nature of the absorption. R.N Jones [33] has summarized characteristic IR group frequencies in a monograph in which a series of six charts and five tables indicate where many groups will be expected to absorb in the IR region.

A given sample may be examined in many ways. It is important to select the technique or accessory, which will give a spectrum from which the required analytical results can be obtained. Having selected the most suitable technique or accessory, care should always be taken to obtain a good quality spectrum, especially when quantitative results are required.

Spectral interpretation is often considered to be as much an art as a science. Psychologists divide us into “visual” or “verbal” people groups. Some analysts “recognize” peak tables, and can start an interpretation simply from the numerical values contained therein. The other groups, possibly more artistic by nature, are those who recognize the patterns within series of spectra, and use these to elucidate structure. Both groups rely heavily on good memory.

2.4.4. Attenuated Total Reflectance

In recent years the technique of Attenuated Total Reflectance (ATR) has become a standard measuring method for Infrared Spectrometry. The technique was also referred to as MIR, or Multiple Internal Reflectance, although this name appears to have gone out of fashion now. It is a surface analysis technique, used mainly when the sample will not transmit infrared radiation, or where it cannot be put into a suitable form for analysis by the standard transmission methods.

In principle the technique relies on the use of a crystal of high refractive index. The crystal is often trapezoidal in shape. The infrared beam enters the crystal normally to one of the short sides. It is then transmitted through the crystal to the adjacent surface. Since the critical angle is exceeded at the crystal/air interface, total internal reflection occurs thus forcing the beam to travel along the length of the crystal being successively internally reflected until it reaches the exit face of the crystal and passes through. At each point of reflection the radiation will interact with any sample, which is placed in contact with the crystal face; and thus a spectrum can be obtained which is similar to a normal transmission spectrum.

ATR refers to what occurs during a single reflection at the sample/crystal interface i.e. the total reflectance at the crystal face is attenuated by the presence of the sample. Most modern work is carried out using a large crystal giving successive, or multiple reflections within the crystal. Other definitions are also used for ATR, but these are based on strict theoretical considerations that are beyond the interest of the average user.

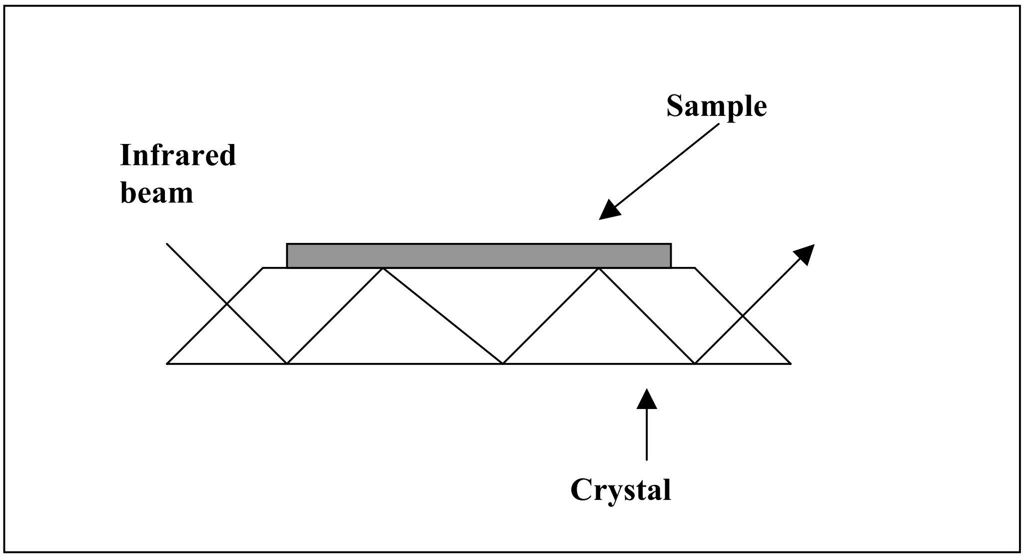


Figure 2.3: The experimental principle of Total Internal Reflectance at the crystal/surface interface are illustrated in this schematic diagram.

However the ATR spectrum is only qualitatively similar to the corresponding transmission spectrum for reasons such as:

- Number of reflections
- Sample size
- Angle of incidence
- Refractive index
- Thickness of sample.

Since ATR is essentially a surface technique, great care was taken to ensure that the crystal was thoroughly cleaned after every analysis. Samples are often difficult to remove, especially from the trough plate of the HATR (Horizontal Attenuated Total Reflectance).

- Chapter 3 -

Residual oil films characterization on the rolled strip

CHAPTER 3.

3.1. Residual oil films on the rolled strip

When rolled with an aqueous emulsion of oil, the strip emerges from the roll bite with its surface covered with a very thin film of the lubricant of the order of a few micrometers thick. The actual thickness of this film depends on the rolling conditions, such as the reduction given to the strip and the work roll diameter. However, it is interesting to note that, even if an emulsion is used, the water phase is generally completely prevented from passage through the roll bite. The residual oil film affords a certain degree of rust protection to the rolled product during the period the coil awaits further processing or during shipment from the plant to the customer. In some instances, the residual oil film is not detrimental in subsequent operations (such as annealing or drawing operations) but in others, its removal is necessary. Where removal occurs either by burn off in annealing furnaces or by electrolytic action in the cleaning tanks, no residues should be left on the strip or, in other words, the oil should possess good “cleanability”.

3.2. Cleanability and burn off characteristics of the lubricant

It would be desirable to leave as thin a film of residual lubricant on the strip after rolling as possible, because where the strip is to be processed further, such film must be either removed or reduced to a low level. However, residual oil film thickness depends on a number of factors such as rolling speed, *type of lubricant*, method of application and the reduction taken. Usually the thickness lies in the range of 1 to 10 grams of oil per square meter. Removal of the oil may be accomplished by several methods. In the case of sheet products, the film may be partly removed by detergent sprays located at the exit end of the mill and then the remainder removed by evaporation during annealing. The elimination of the rolling oil that remains attached to the steel surface leads to the formation of carbon residues that should be kept at low levels to obtain a clean surface. For strip used in tinplate manufacture, removal of the oil is usually accomplished by electrolysis using an alkaline cleaning solution.

3.3. Analysis of residual oil on cold rolled material

Contaminants remaining on the steel sheet after processing can influence the performance of the customer's fabricated products. Steel producers continually carry out monitoring and development work to ensure that contaminants on the finished steel surface are kept to a minimum. One class of contamination is carbonaceous matter. This can arise from the final processing stages of the steel sheet, i.e., pickling (where a protective oil is applied), cold rolling (where 2% oil-in-water emulsions are used as lubricants and coolants) and annealing (where the extent to which oily matter is volatilized influences the residuals). In order to determine the cause or causes responsible for the poor oxidation stability of the oils obtained on samples from the cold rolling line tests, detailed surface residues analysis were performed on cold rolled material. Such surface analyses would determine the different chemical species found on the surface. The first objective with these analyses was to determine if a common surface composition denominator existed between the current used oil and the unsaturated oil. To demonstrate these results, representative spectra are presented in Figure **3.1** and Figure **3.2**.

Contaminants remaining on the steel sheet after processing can influence the performance of the further processing of the product. Steel producers continually carry out monitoring and development work to ensure that contaminants on the finished steel surface are kept to a minimum. The band assignments [34] of the neat vegetable-based oil (Fig. **3.1**) is shown in Table **III**. Comparison of the neat vegetable-based oil with the oil residues was done. The infrared spectrum of the oil residues (Fig. **3.2**) shows the absorbed water (3421 cm^{-1} and 1596 cm^{-1}), (the oils are used as an emulsion solution of 2-5%), broadening of the ester band (1744 cm^{-1}), and the difference in composition of the additives around the fingerprinting region (1200-900 cm^{-1}), due to the degradation or depletion of additives. Broadening of the ester band shows the presence of oxidation products. These findings are explained in more details in Chapter 4.

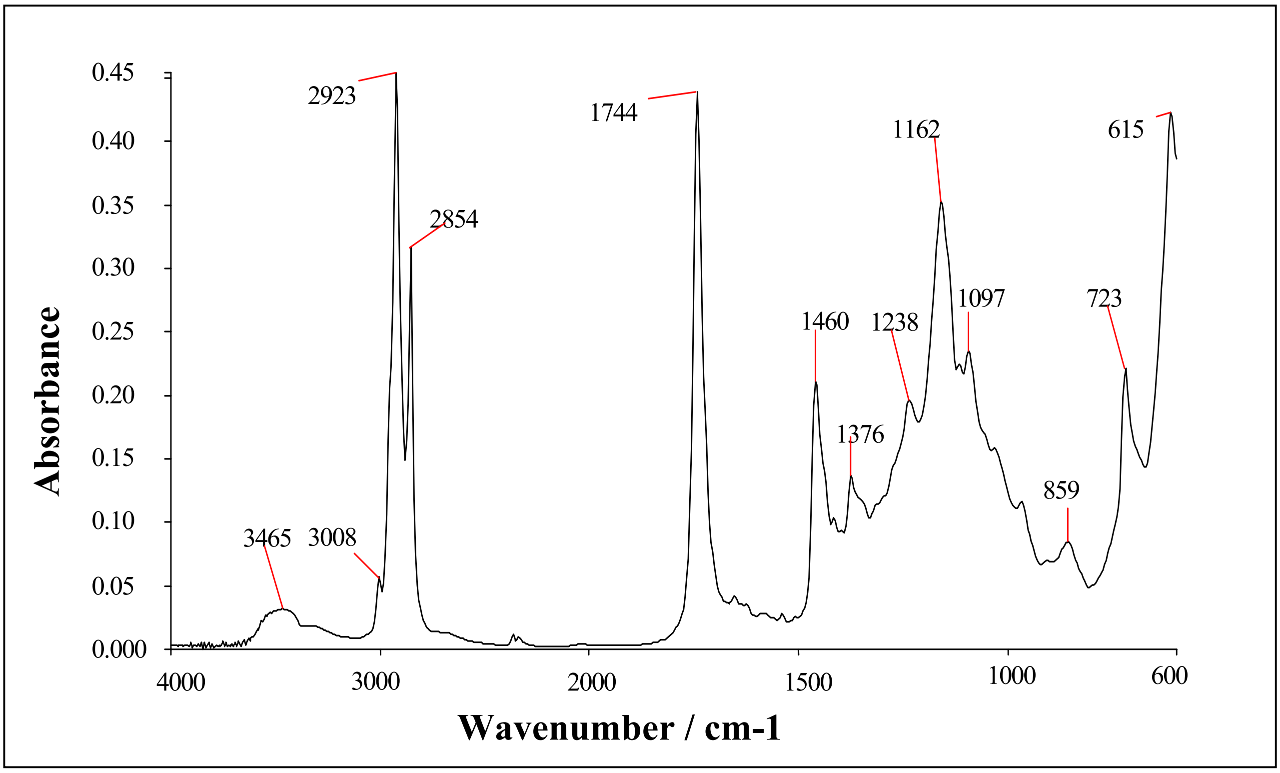


Figure 3.1: Infrared spectra of neat unsaturated oil used on the cold rolling mill.

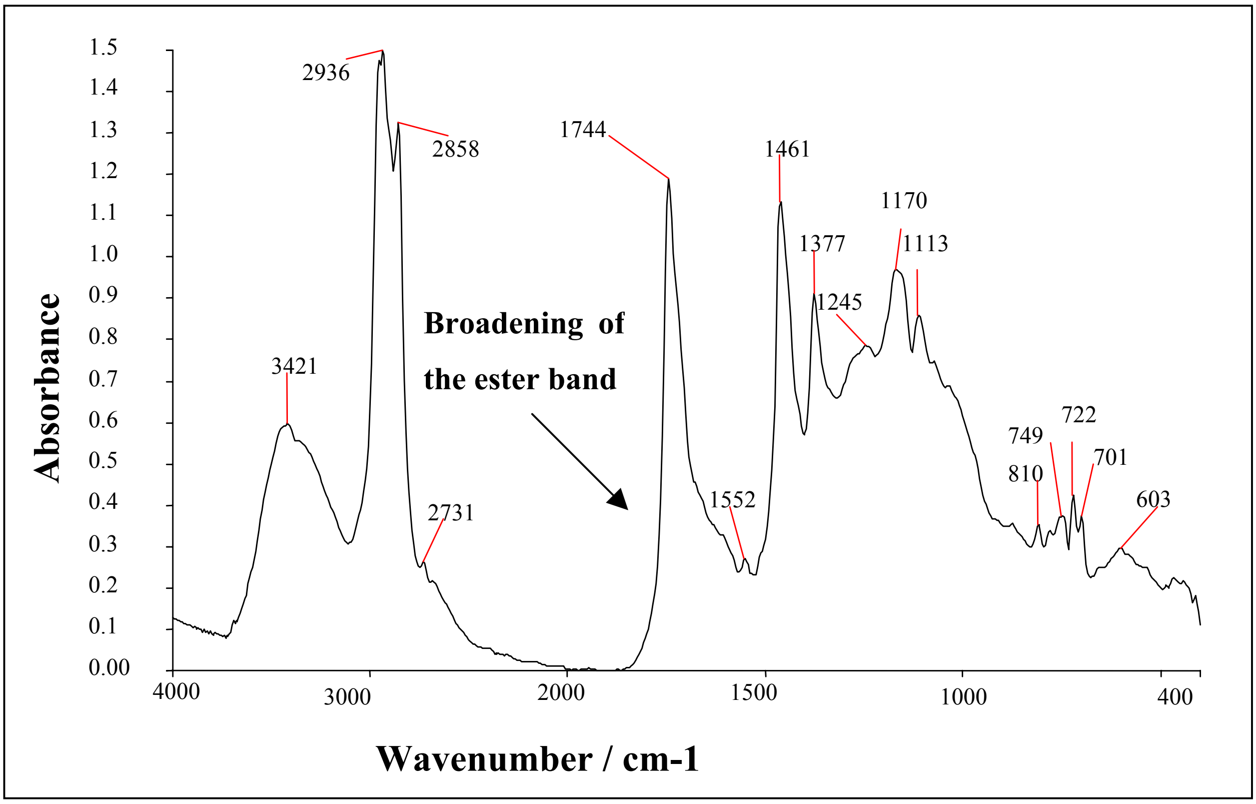


Figure 3.2: Infrared spectra of oil residues left on the surface of the steel after cold rolling process.

3.4. Assignment of infrared bands of rolling oils

The assignments of the characteristic infrared bands of base oil and ester components of rolling oil are shown in Table **III** below.

Table III

IR vibrational assignments of rolling oil [34]

Composition of Rolling oil	Band position (cm^{-1})	Intensity	Assignment
Base oil - Aliphatic components	3100-3000	m	C-H stretch adjoining C=C
	3000-2800	s	CH and CH stretching
	1460	m	CH and CH deformation
	1378	m	CH deformation
	720	w	CH rocking in long chains
Base oil - Aromatic components	3100-300	sh	C-H aromatic stretch
	1605	w	Aromatic ring stretching
	865	s	Out of plane vibration of single hydrogen on aromatic ring
	815	s	Out of plane vibration of two adjacent hydrogens
	750	s	Out of plane vibration of four adjacent hydrogens
Esters	3520	w/m	Free -O-H
	2500-3300	m	Stretching of hydrogen bonded to O-H group, overlap with H2O
	3400-2600	m	O-H stretch of an acid
	3470	w	Overtone of C=O ester stretch
	3008	m	C-H stretch of unsaturated acid component
	3000-2800	s	CH and CH stretch overlap with base oil
	1745	vs	C=O stretch of an ester
	1710	vs	C=O stretch of an acid
	1656	w	C=C stretch of unsaturated acid component
	1460	m	CH and CH deformation, overlap with base oil
	1378	w	CH deformation, overlap with base oil
	1170	s	C-O stretch of an ester group
	1120-900	m/w	Other less intense absorptions of ester.
	720	w/m	CH rocking in long chains

- Chapter 4 -

Experimental procedures and the influence of unsaturated oils on surface composition of cold rolled material

CHAPTER 4.

4.1. Rolling oil with polyunsaturated fatty acids

4.1.1. Overview

Atmospheric oxidation is the most important cause of deterioration in lubricants [35]. This oxidative rancidity is accelerated by exposure to heat, light, humidity and the presence of trace metals. The intense rolling of steel with the oil used as lubricant causes an oxidizing thermal degradation with formation of decomposition products, and change in physical properties such as colour and odour. When oxygen travels through oil, it is absorbed by the oil and reacts mainly with the C=C double bond, thus the polyunsaturated components of the oil oxidize much faster than saturated ones. Spectroscopic methods can be employed to evaluate deterioration in oils subjected to heat. Fourier transform infrared spectroscopy (FTIR) provides a quick and accurate way of evaluating thermal degradation in these lubricants.

4.1.2. Oxidation of rolling oils and polyunsaturated fatty acids

The oxidative deterioration of polyunsaturated fatty acids in cold rolling oils has been monitored by Fourier transform infrared spectroscopy (FTIR). The thermal oxidation of polyunsaturated fatty acid is a free radical chain reaction, in which hydroperoxides are generally recognized as the primary major product [36]. The hydroperoxides of the polyunsaturated fatty acids are easily decomposed into a very complex mixture of secondary products with the decrease in saturation. The oxidative advance of unsaturated fatty acids during heating was studied by the determination of non-saturation at different temperatures and heating times.

4.1.2.1 Experimental

(a) Instrumentation

FT-IR spectra were obtained using a Perkin Elmer GX spectrum 2000 Fourier Transform Infrared Spectrometer with a ZnSe horizontal ATR accessory. Fifteen scans were recorded over the frequency range 4000-400 cm^{-1} and Fourier transformed to give a resolution of 8 cm^{-1}. Data acquisition and processing made use of software Spectrum version 2 for Windows, Perkin Elmer.

(b) Samples

Typical cold rolling oil formulations (Vegetable-based oil) and steel samples with oil residues on the surface were obtained from an industrial supplier. The pure typical rolling oil components (Oleic acid, Palmitic acid, Stearic acid, Myristic acid and Lauric acid) were from MERCK chemicals.

(c) Procedure

Oxidation in oil

Approximately 80 ml of a vegetable-based rolling oil and each of the fatty acids were placed in petri dishes heated in a furnace. To follow the oxidation process in the oil during rolling, sample temperatures were increased to 350˚C. During this process heating was maintained for 45 minutes at the following temperatures: 100˚C, 150˚C, 200˚C, 250˚C, 300˚C, and 350˚C.

FTIR analysis

To analyse the IR spectra of the vegetable-based temperature treated rolling oil and fatty acids samples, absorbance was measured as band intensity at 3008 cm^{-1} with respect to the base line tangent at 3113 – 2720 cm^{-1}, at 970 cm^{-1} with respect to the base line at 990-944 cm^{-1} and the band at 2200 cm^{-1}, corresponding to no peak. In these samples, the absorbance quotient A (3008)/A (2200) and A (970)/A (2200) was measured with respect to the same base lines to obtain the calibration straight line.

4.1.2.2 Results and discussions

(a) Thermally oxidized vegetable- based oil

The infrared spectrum of the oxidized vegetable oil (Fig. **4.1**) shows the broadening of the ester band (1745 cm^{-1}), and the difference in composition of the additives around the fingerprinting region (1200-900 cm^{-1}). Broadening of the ester band shows the presence of oxidation products. These changes were also observed in (Fig **3.2**) chapter 3.

The infrared spectra of vegetable-based rolling-oil samples heat treated at six different temperatures (100˚C, 150˚C, 200˚C, 250˚C, 300˚C, and 350˚C) are shown by Figure **4.2a**. The infrared spectrum of the vegetable-based rolling oil shows no absorbance band at 2200 cm^{-1}, which was used for normalization, as it does not interfere with any of the sample bands. The band at (3008 cm^{-1}) is due to C-H stretching vibration associated with the cis isomer at the C=C double bond [34] (Fig. **4.2b**). This band can be seen at ambient temperatures and decreases in intensity as the temperature increases. The vegetable-based rolling oil gives rise to a band at 967 cm^{-1} with an increase in temperature. This band (C-H) was assigned to the trans isomer of the unsaturated non-conjugated C=C double bond (Fig. **4.2c**) [35]. The values obtained to draw up calibration lines representing the quotient A (3008)/A (2200) and A (967)/(2200) against temperature are shown in Table **IV** and **V** respectively. These results are shown graphically in Figure **4.3**.

The linear regression provided a correlation coefficient of 0.997 with respect to the cis isomer of the unsaturated double bond (3008 cm^{-1}) and a correlation coefficient of 0.983 with respect to the trans isomer of the unsaturated double bond (967 cm^{-1}) for the six samples.

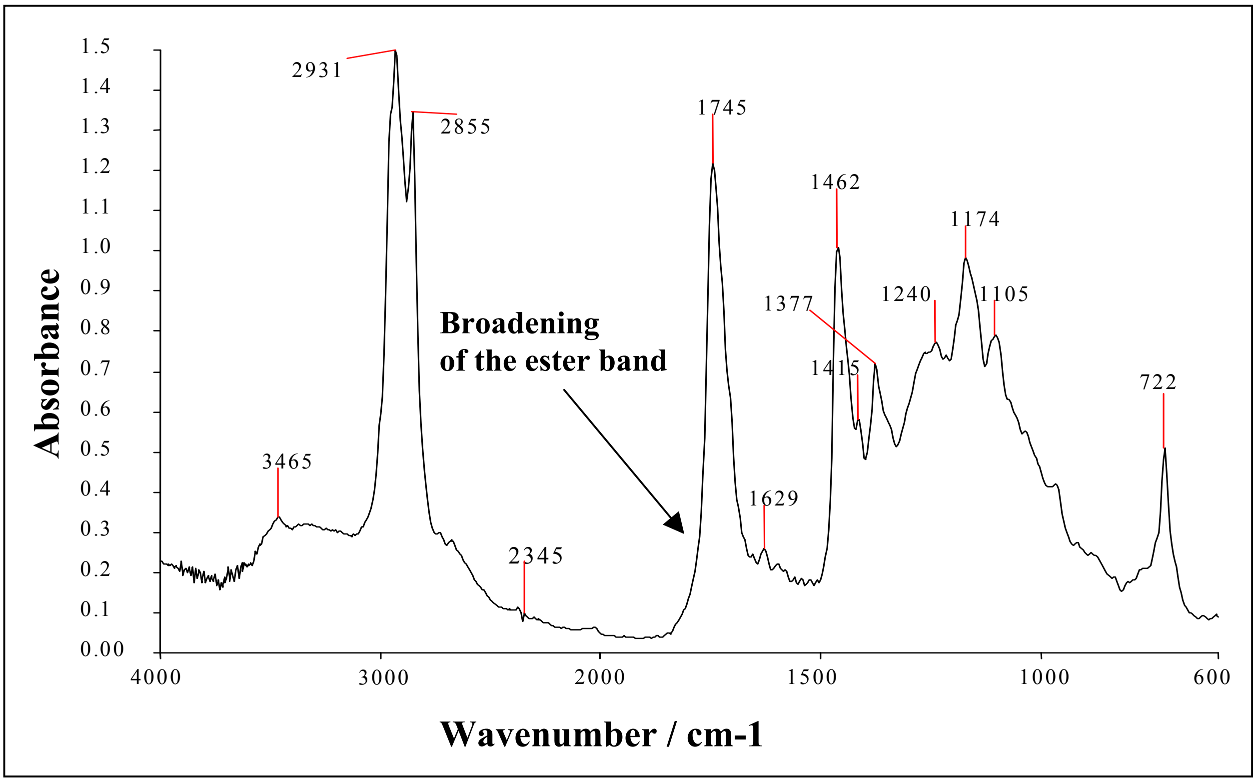


Figure 4.1: Infrared spectrum of the thermally oxidized vegetable-based rolling oil heated to ≈350˚C.

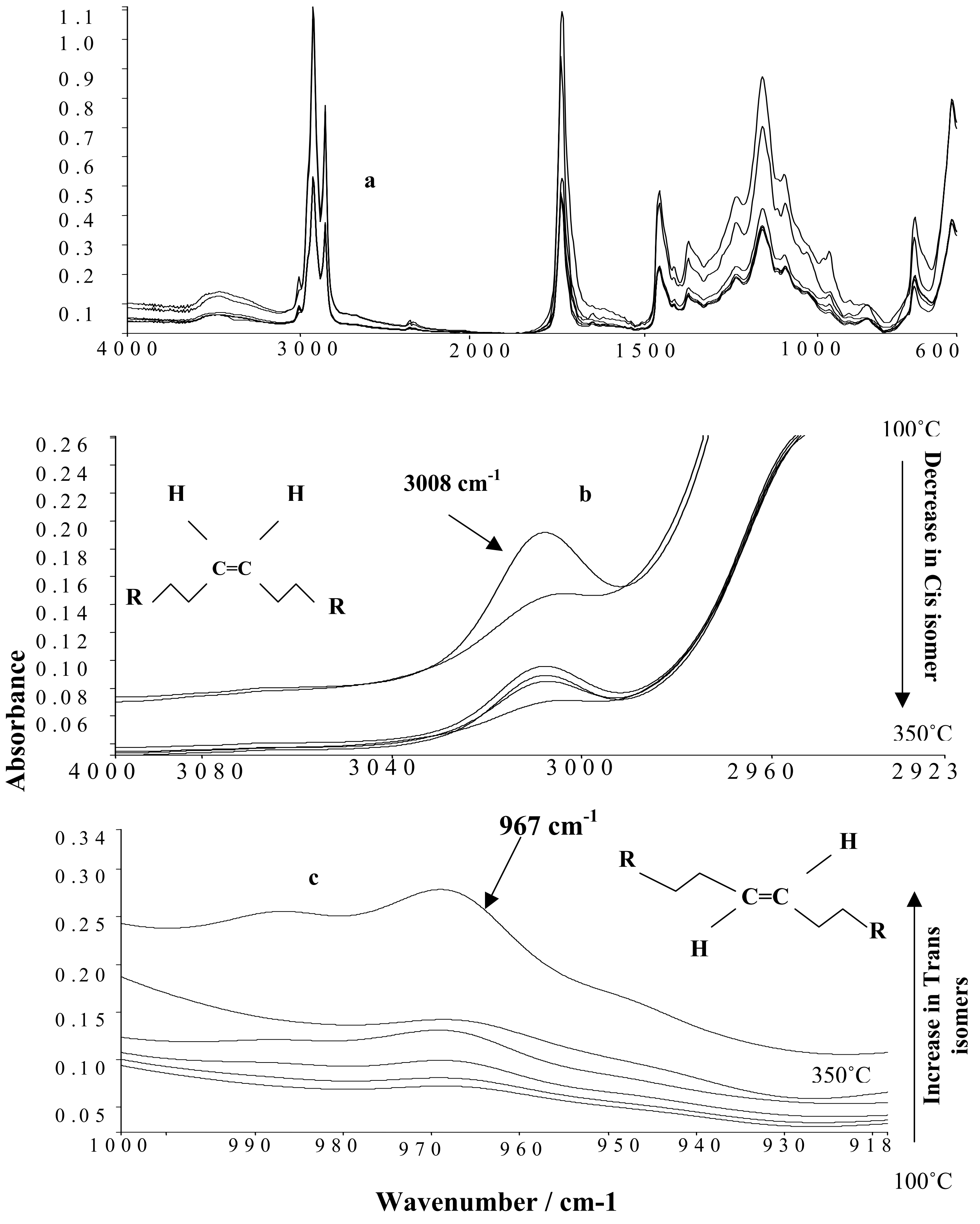

1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
a
4000
3000
2000
1500
1000
600
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
H
H
C=C
R
R
3008 cm-1
b
100˚C
Decrease in Cis isomer
350˚C
Absorbance
4000
3080
3040
3000
2960
2923
967 cm-1
c
R
H
C=C
H
R
0.34
0.30
0.25
0.20
0.15
0.10
0.05
350˚C
Increase in Trans isomers
1000
990
980
970
960
950
940
930
918
100˚C
Wavenumber / cm-1

Figure 4.2: Infrared spectra of a vegetable based rolling oil.

a - Infrared spectra of a vegetable based rolling oil previously heated to 100˚C, 150˚C, 200˚C, 250˚C, 300˚C and 350˚C (from top to bottom).

b - Infrared spectra showing the band used to determine the unsaturated double bond (3008 cm^{-1}). This band is due to the stretching of the C-H bond adjoining the double C=C bond.

c - Infrared spectra showing the band (968 cm^{-1}) of the isolated C=C double bond with trans configuration.

Table IV

Total height of the cis configuration of the unsaturated double bond (3007 cm^{-1}) band with an increase in temperature

Temperature (°C)	Total height (3007 cm-1)	Total height (2200 cm-1)	A (3007)/ A (2200)
100	0.1849	0.0167	11.07
150	0.1809	0.0194	9.32
200	0.1768	0.0243	7.28
250	0.1251	0.0252	4.96
300	0.0492	0.0183	2.69
350	0.07	0.005	14.00

Table V

Total height of the trans configuration of the unsaturated double bond (967 cm^{-1}) with an increase in temperature

Temperature (°C)	**Total height (2200 cm-1)**	**Total height (967 cm-1)**	**A (967)/ A (2200)**
100	0.0167	0.0484	2.89
150	0.0194	0.0845	4.35
200	0.0243	0.106	4.63
250	0.0252	0.1566	6.21
300	0.0183	0.1409	7.69
350	0.005	0.1108	22.16

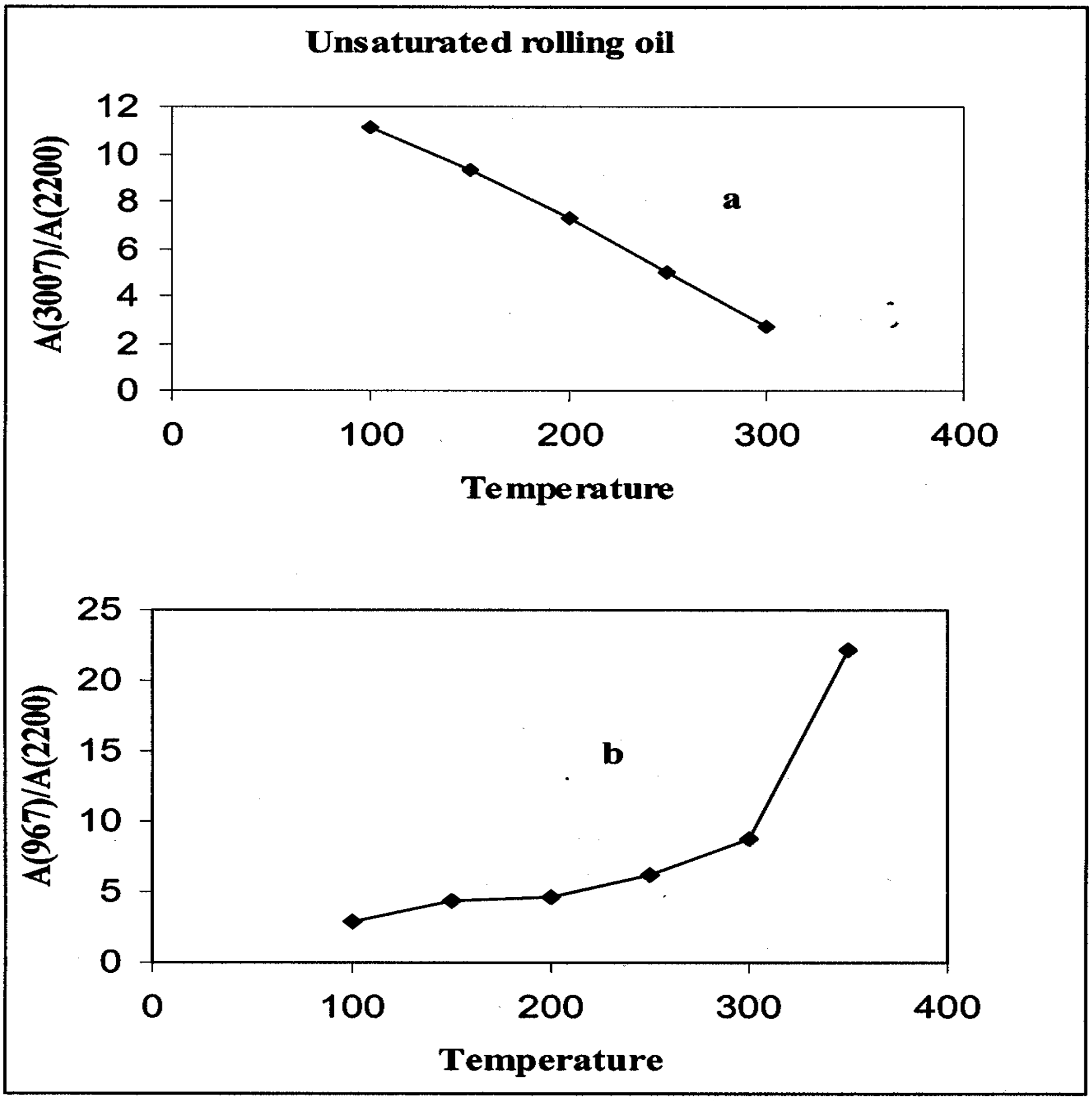


Figure 4.3: The calibration line of the vegetable based rolling oil.

a - The graph showing decrease in unsaturated double bond compound (3007 cm^{-1}) with an increase in temperature.

b - The graph showing an increase in trans isomer (967 cm^{-1}) with increase in temperature.

(b) Cis – trans rearrangement

A comparison between the unsaturated acid (oleic acid) and the saturated acid (palmitic acid) was necessary to confirm the formation of the trans isomer. This comparison is shown in figures **4.4** and **4.5.** The IR spectra of oleic acid (Fig. **4.4**) shows the C-H band at 965 cm^{-1}, which is characteristic of the trans isomer of the unsaturated non-conjugated C=C double bond. The same band was observed in vegetable-based rolling oils. No significant changes were seen with the saturated acid (palmitic acid, Fig.**4.5**). The results for stearic acid, myristic acid and lauric acid are not shown, as they are similar to that of the palmitic acid.

The cis isomer of the unsaturated double bond compound can be seen for the vegetable-based rolling oil and the oleic acid, at ambient temperature. The results show that the cold rolling process causes a decrease in the cis isomer and an increase in the trans isomer. In all the oils studied, degradation becomes considerable after 150ºC. A significant decrease in cis isomer, approximately 70%, is apparent at high temperature. The reason for the thermal and oxidative instability of the vegetable-based rolling oils is the unsaturated double bond in the fatty acid.

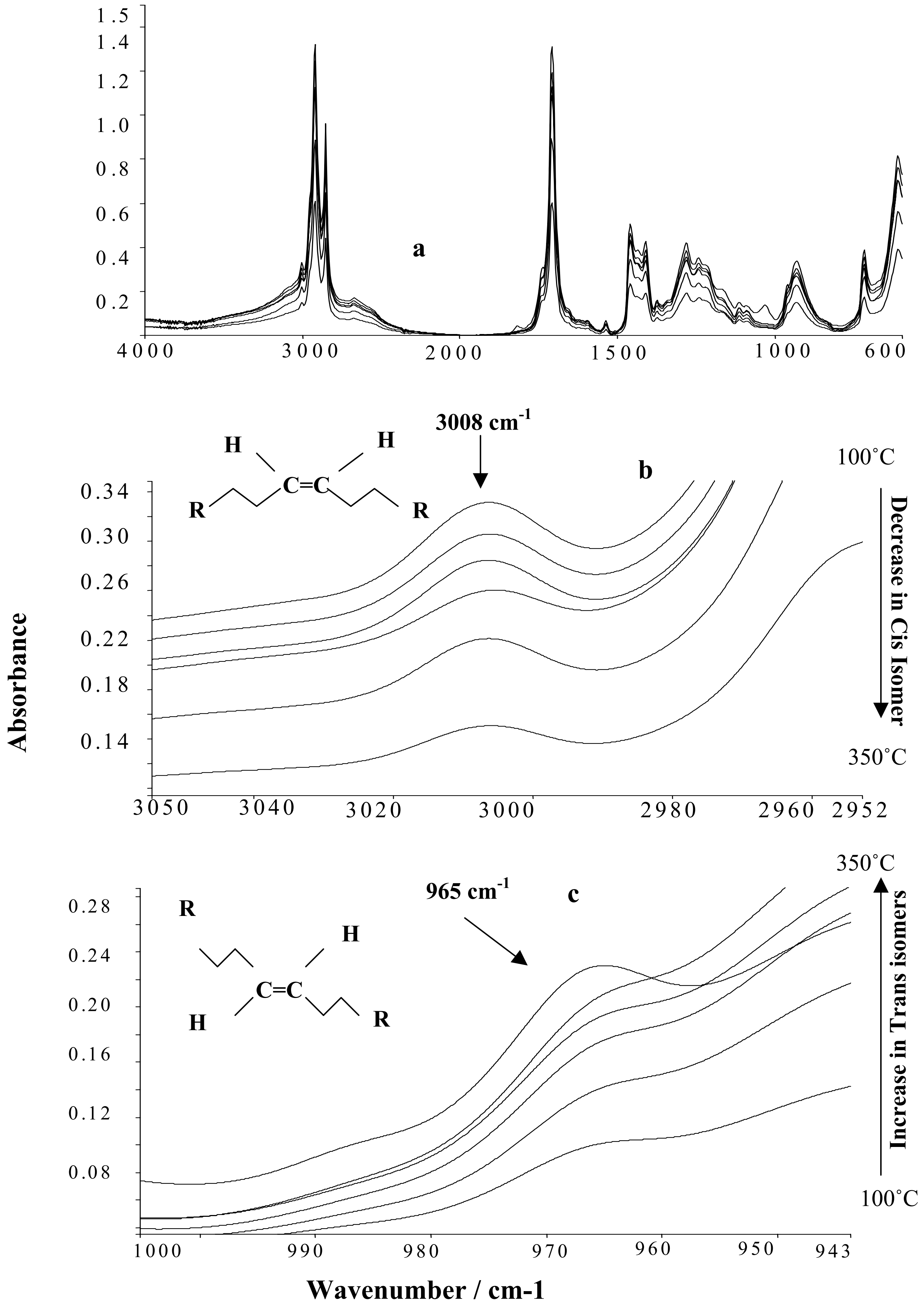

1.5
1.4
1.2
1.0
0.8
0.6
0.4
0.2
a
4000
3000
2000
1500
1000
600
3008 cm-1
H
H
C=C
R
R
b
100°C
Decrease in Cis Isomer
350°C
Absorbance
0.34
0.30
0.26
0.22
0.18
0.14
3050
3040
3020
3000
2980
2960
2952
350°C
965 cm-1
c
R
H
C=C
H
R
Increase in Trans isomers
100°C
0.28
0.24
0.20
0.16
0.12
0.08
1000
990
980
970
960
950
943
Wavenumber / cm-1

Figure 4.4: Infrared spectra of oleic acid – example of an unsaturated compound.

a - Infrared spectra of Oleic acid previously heated to 100˚C, 150˚C, 200˚C, 250˚C, 300˚C and 350˚C (From top to bottom).

b - Infrared spectra showing the band used to determine unsaturated double bond cis compound (3008 cm^{-1}). This band is due to the stretching vibration of the C-H bond adjoining the double C=C bond.

c - Infrared spectra of the band (965 cm^{-1}) of isolated double C=C bond with trans configuration.

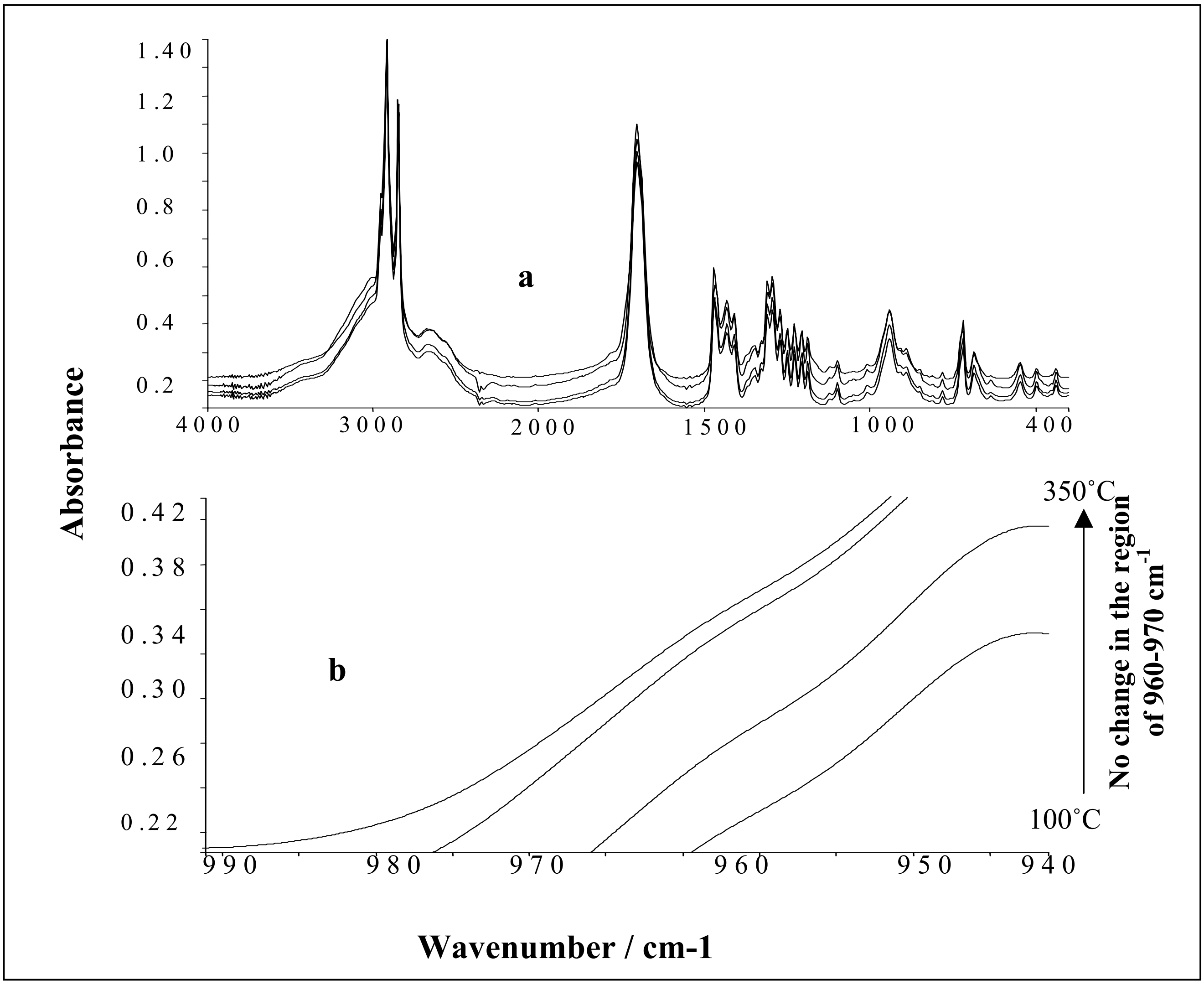


Figure 4.5: Infrared spectra of Palmitic acid – example of a saturated compound.

a - Infrared spectra of Palmitic acid previously heated to 100˚C, 150˚C, 200˚C and 250˚C (from bottom to top).

b - Infrared spectra of Palmitic acid showing no change at 965 cm^{-1}.

4.2. Influence of free fatty acids and bonded fatty acids

Pickling and rolling oils commonly contain esters of fatty acids with a mineral oil base. Free fatty acids in these systems can react with the steel surface to form iron soaps. Free fatty acids polymerize more easily than bonded fatty acids. The iron soaps contaminate the rolling oil bath and detract from steel surface cleanliness. Iron soaps can act to thicken the oil film in the roll bite by increasing the viscosity of the rolling oil, and accelerate the roughness reduction. Additionally, Fe soaps are used to create a strong oiliness improving effect, so they prevent the metal contact between roll and strip asperities, and restrain the roughness re-creation by scoring. The surface cleanliness before coating is a major parameter for producing coated steel sheet with good properties in terms of adherence and appearance. So, all the coating lines have a pretreatment section with a cleaning bath (with or without electrolysis), and electrodeposition lines have in addition a pickling tank (Zn, ZnNi, Sn, Cr). In fact, the pretreatment section depends on the surface contamination. For hot dip galvanized products, the steel sheet comes directly from cold rolling. So the surface is contaminated with iron fines generated by friction between the steel sheet and the rolls, oil residues that commonly are the result of reaction between oil and surface (free fatty acids, iron soaps, esters, and sulfates residues coming from additives, like phosphates). This contaminates could cause delamination or adhesion problems during the electro galvanizing to the cold rolled steel material.

- Chapter 5 -

Conclusions

CHAPTER 5.

5.1. Conclusions from previous literature

The aim of this dissertation was to determine the cause or causes of poor steel surface cleanliness with respect to cold rolling oils oxidative stability from a specific production line. In broad terms, the literature study revealed the following:

(a) that the poor steel surface cleanliness was as a results of carbonaceous matter left on the steel surface after rolling [10];

(b) that the oil/surface interaction species were the determining factor in interpreting the steel surface cleanliness [11];

(c) that the components in the rolling oil determine rolling oil properties [5, 6, 7];

(d) that the mechanism by which the oil oxidizes is by a free radical that leads to the formation of peroxy and epoxy intermediate, which eventually produce a variety of oxidation products, such as free fatty acids, aldehydes and ketones [22].

To define further areas of study, a more detailed summary of the results are given.

5.2. Summary of the current results

FTIR Spectroscopy provides very useful information on the composition and the extent of thermal oxidation in cold rolling oils. The methodology developed in this study permitted determination of the percentage of unsaturated components in the samples at different temperatures. The use of absorbance quotient measurements permitted quantitative analysis without requiring a constant and known cell thickness which facilitates sample handling and reducing analysis time. Furthermore, it permits quantification in cases where it is impossible to know the optic path-length accurately.

The trans isomer observed in the rolling oil was due to changes in the unsaturated fatty acids. It can be said that when an unsaturated rolling oil is subjected to a heating process, the initial nature of the oil changes significantly and the decrease in unsaturated compound and increase in the trans isomer is evidence of the transformation occurring in the essential polyunsaturated fatty acids which the oil initially contains, thus indicating a decrease in the oil's performance capacity. The determination of unsaturated double bond compounds in rolling oils makes it possible to classify them and evaluate their oxidative deterioration which can be directly related with the unsaturated fatty acids.

5.3. Conclusions

Relating to the production environment of the cold rolling process, the following conclusions were reached, namely:

(a) If the process currently used on the cold rolling mill remains the same, the poor steel surface cleanliness of the steel produced on that line must be taken as characteristic of rolling oil used on that line.

(b) The determination of unsaturated compounds in rolling oils makes it possible to classify them and evaluate their oxidative deterioration which is directly related with the degradation of polyunsaturated fatty acids in the oils.

(c) Although detergent at the exit of the line can remove most of the oil residues, the oil/surface interaction species still remains in trace amount after annealing (Figure 1.2 [20, 21]).

- References -

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- Appendix A -

The paper submitted to Journal of Vibrational Spectroscopy

February 2004

Appendix A

Optimization of rolling mill oil evaluation using FT-IR spectroscopy

Pheladi Junior Mogwaneng1, Danita de Waal2a and Jan CA Boeyens2

1 Industrial Metals and Minerals Research Institute (IMMRI), University of Pretoria,
Republic of South Africa
2 Department of Chemistry, University of Pretoria, 0002, Pretoria
Republic of South Africa

Abstract

The performance of vegetable-based rolling oils was investigated by recording the FTIR spectra of the oils using Horizontal Attenuated Total Reflectance, an internal reflection accessory, before and after systematic heat treatment. Evidence was found that the vegetable-based oils degraded on heating and the spectroscopic analysis indicated that this was due to rearrangement of unsaturated components from cis to trans configuration.

Keywords: Vegetable-based rolling oils; Unsaturated fatty acids; Trans fatty acids; Infrared spectroscopy.

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[a] Author to whom correspondence should be sent. E-mail: danita.dewaal@up.ac.za

Introduction

Although rolling lubricants are sold commercially under brand names, basically their constituents are selected from oils, fats and waxes. Prior to World War II, palm oil was the most widely used rolling lubricant but the shortage of the imported lubricant spurred the search for substitute materials. This search led to the use of tallow and a large number of other organic materials presently in use today, many of which are blended with other materials such as emulsifiers, defoamers, antioxidants, and rust inhibitors[1].

Generally speaking, palm-oil substitutes (derived from vegetables and animal oils), for use as cold rolling lubricants, are esters of the trihydric alcohols, glycerol, with such saturated fatty acids as lauric, myristic, palmitic and stearic. These esters are called glycerides. In addition, esters of unsaturated acids of the acrylic series, such as oleic acid, are usually present in the vegetable oils. Although cold-rolling lubricants have been extensively used as far back as the early 1930's, research into cold-rolling lubricant behaviour was not undertaken to any significant extent until the late 1940's. Even then, for a variety of reasons, the research data were often difficult to interpret or relate to other rolling specifications. It can be understood that poor steel surface cleanliness experienced as a result of the use of rolling lubricants, have plagued the steel industry for as long as oils were used. Previous research on the oxidative stability of edible oil has been reported(2-6), although few studies on the oxidative stability of rolling oils are in literature. Werner Lueg and Paul Funke[7] reported rolling tests with commercial rolling oils under different operating conditions. Many oil compositions and methods of evaluation have been considered. Several traditional physical and chemical laboratory tests, listed in Table I, are available to determine pertinent properties of process and rolling oils. Tanikawa and Fujioka[8] reported an approach for the clarification of the lubrication performance of cold rolling oil using the analytical methods of

HPLC, gel permeation chromatography, GC, IR and GC-MS. These methods were utilized to investigate reaction products such as free and iron-soap-forming fatty acids, and to determine their chain length and degree of unsaturation.

Our research aims to develop rapid, general-purpose Fourier Transform Infrared (FTIR)-based quality control method for the rolling oil industry. The rationale for turning to a new version of an old technology, IR, is that FTIR spectrometers have many advantages over a conventional dispersive instruments, with more energy throughput, excellent wavenumber reproducibility and accuracy, extensive and precise spectral manipulation capabilities (ratioing, subtraction, derivative spectra and deconvulation) and advance software to handle calibration development[5]. Because of these advantages, FTIR spectroscopy can provide much more information on the characteristics, composition and/or chemical changes taking place in fats and oils than can be obtained from conventional dispersive IR instrument. From a practical viewpoint, FTIR quantitative analysis are generally rapid (1-2 min), can reduce the need for solvents and toxic reagents associated with wet chemical methods for fats and oils analysis, making the development of FTIR method timely in view of present efforts to eliminate toxic solvents[9].

The overall objective of this work is to lay the foundation for the development of FTIR methods for assessing oil quality in relation to oil oxidation and thermal stress (e.g., systematic heating). A prerequisite to using FTIR spectroscopy to assess the various end products of oil oxidation is a basic understanding of the spectral changes taking place as oil oxidizes. Fundamental IR characterizations and identifications of specific products formed from the oxidation of individual fatty acids and the decomposition of fatty acids hydroperoxides has been done[10-11], but there have been no comprehensive FTIR spectroscopic investigations of rolling oils undergoing oxidation. Thus there is a need to characterize the spectral changes occurring as rolling oil oxidation proceeds, assign wavelengths to the more common molecular species produced so that a generalized approach to products associated with oxidation can be developed. This paper describes the FTIR spectral technique used to follow the main chemical events occurring as rolling oil oxidizes.

Experimental

Instrumentation

The instrument used for this work was a Perkin-Elmer Spectrum GX FTIR spectrometer (Norwalk, CT USA), with a room temperature deuterated triglycine sulphate (DTGS) detector. A horizontal ATR sampling accessory, equipped with ZnSe crystals was used in this study. All spectra were collected from 15 scans at a resolution 8 cm^{-1} and a gain of 1.0 over the frequency range 4000-400 cm^{-1}. Spectra were ratioed against the background air spectrum.

Samples/oxidation

Typical cold rolling oil formulations (Vegetable-based oil) and steel samples with oil residues on the surface were obtained from an industrial supplier. Commercial rolling oil components (Oleic acid, Palmitic acid, stearic acid, Myristic acid and Lauric acid) were obtained from MERCK chemicals and used as the base material for the oxidation studies.

Two sets of oxidation experiments were carried out, one at higher temperature ≈ 400˚C (this temperature was chosen in light of the mechanical nature of the cold rolling process, and friction that can cause temperature increase to ≈ 400˚C) and another at lower temperatures 100˚C, 150˚C, 200˚C, 250˚C, 300˚C, and 350˚C. For the ATR work, ≈ 1ml of neat vegetable-based oil sample was pipetted onto the crystal (surface are ≈ 8 cm^2), and its single-beam spectrum was recorded and ratioed against a single-beam of air (clean crystal surface). For the higher temperature (≈ 400˚C) oxidation, 80 ml of oil was placed in petri dish heated in a furnace and maintained for 45 minutes. A single-beam spectrum of the oil was collected. For the lower temperature (100˚C, 150˚C, 200˚C, 250˚C, 300˚C, and 350˚C) oxidation, single-beam spectra were subsequently recorded at each temperature from these samples (vegetable based oil and the fatty acids) as they oxidize.

FTIR analysis

To analyse the FTIR spectra of the vegetable-based temperature treated rolling oil and fatty acids samples, absorbance was measured as band intensity at 3008 cm^{-1} with respect to the base line tangent at 3113 – 2720 cm^{-1}, at 970 cm^{-1} with respect to the base line at 990-944 cm^{-1} and the band at 2200 cm^{-1}, corresponding to no peak. In these samples, the absorbance quotient A (3008)/A (2200) and A (970)/A (2200) was measured with respect to the same base lines.

Results and discussions

The concept of spectral ratioing

One of the fundamental strengths of FTIR spectroscopy lies in its ability to accurately ratio spectra, allowing one to see small differences that normally might not be apparent in the raw spectrum. The concept of spectral ratioing arises in FTIR spectroscopy because most FTIR spectrometers are single-beam instruments. When Fourier Transform Infrared (FTIR) spectrometers such as Spectrum GX record spectra, the data they record is characteristic of both the sample (I_S) and the spectrometer (the source, detector, beamsplitter, and window material all contributes to the spectrum). Also, any infrared-active species in the optical path (in particular, atmospheric CO_2 and water vapour) add to the spectrum. To remove the instrument and the air background, the single-beam spectrum of the sample is ratioed against a single-beam spectrum recorded with no sample in the beam (I_0), yielding the absorbance spectrum of the sample [$A_S = -\text{Log}\,(I_S/I_0)$].

Figure 1 shows the spectrum in the frequency region 4000-400 cm^{-1} of vegetable-based oil in its neat form on an ATR crystal, obtained by ratioing the single-beam spectrum of the oil against the single-beam spectrum of air (bare crystal surface). This spectrum illustrates the dominant spectral features associated with vegetable based oils[12], the band assignments[13] are shown in Table II

Figure 2 is the spectrum of the same oil collected on the steel surface after rolling process. The oil residues were washed off with petroleum ether and the extraction took place during 20 minutes. The products left on the steel, which were not extractable in petroleum ether, were not investigated. This spectrum shows the O-H stretching vibration (3421 cm^{-1}); an O-H bending vibration of water (the oils are used as an 2-5% emulsion solution) overlapping with the carbonyl band 1750-1600 cm^{-1}. Further more the water bands can overlap with the bands of other components. The presence of water can be established by comparing the intensity of the water-overlapping band to that of the higher frequency component of the water band and/or the other characteristic absorption of water at 1625 cm^{-1} (not shown). The bands that correspond to C-H stretching and bending vibrations were clearly seen between 2970-2845 cm^{-1} and 1460-1370 cm^{-1} respectively. The carbonyl functional group of oil in the FTIR spectra is in the region of 1750-1600 cm^{-1}. The broadening of the carbonyl band C=O (1750-1600 cm^{-1}) in Fig. 2 was due to the formation of the free fatty acids and may overlap with absorption band of the ester carbonyl functional group of the oil, which is in the range 1748-1746 cm^{-1} [14]. Oxidative conditions can lower the frequency to 1743 cm^{-1} depending on the appearance of carbonyl absorbencies of saturated aldehydes[15]. As the oil oxidized at ≈ 400˚C, one can clearly see, from left to right in Figure 3: (i) the appearance of a broad band in the OH stretching region (3800-3200 cm^{-1}), (ii) the disappearance of the C-H terminal stretch C=C band[16] (3008 cm^{-1}), (iii) the broadening of the band on the low frequency side of the ester linkage absorption and (iv) a rise in band in the trans double bands region (1000-900 cm^{-1}). All this bands in Figure 3 are an ambiguous indication of the production of new molecular species. The initial oxidation products that accumulate in triacylglycerols are hydroperoxides, which may subsequently break down to form lower-molecular weight compounds, such as alcohols, aldehydes, free fatty acids; and ketones, ultimately leading to rancid product[17].

The infrared spectra of vegetable-based rolling-oil samples heat treated at six different temperatures (100˚C, 150˚C, 200˚C, 250˚C, 300˚C, and 350˚C) are shown by Figure 4a. The infrared spectrum of the vegetable-based rolling oil shows no absorbance band at 2200 cm-1, which was used for normalization, as it does not interfere with any of the sample bands. The band at (3008 cm^{-1}) is due to C-H stretching vibration associated with the cis isomer at the C=C double bond [16] (Fig. 4b). This band can be seen at ambient temperatures and decreases in intensity as the temperature increases. The vegetable-based rolling oil gives rise to a band at 967 cm^{-1} with an increase in temperature. This band (C-H) was assigned to the trans isomer of the unsaturation of non-conjugated C=C double bond (Fig. 4c) [18]. The values obtained to draw up calibration lines representing the quotient A (3008)/A (2200) and A (967)/(2200) against temperature are shown in Table III and IV respectively. These results are shown graphically in Figure 5.

The linear regression provided a correlation coefficient of 0.997 with respect to cis isomer of the unsaturation (3008 cm^{-1}) and a correlation coefficient of 0.983 with respect to trans isomer of the unsaturation (967 cm^{-1}) for the six samples.

Cis – trans rearrangement

A comparison between the unsaturated acid (oleic acid) and the saturated acid (palmitic acid) was necessary to confirm the formation of the trans isomer. This comparison is shown in figures 6 and 7. The IR spectra of oleic acid (Fig. 6) shows the C-H band at 965 cm-1, which is characteristic of the trans isomer of the unsaturation of non-conjugated C=C double bond. The same band was observed in vegetable-based rolling oils. No significant changes were seen with the saturated fatty acid (palmitic acid, Fig.7). The results for stearic acid, myristic acid and lauric acid are not shown, as they are similar to that of the palmitic acid. The cis isomer of the unsaturation can be seen for the vegetable-based rolling oil and the oleic acid, at ambient temperature. The results show that the cold rolling process causes a decrease in the cis isomer and an increase in the trans isomer. In all the oils studied, degradation becomes considerable after 150ºC. A significant decrease in cis isomer approximately 70% is apparent at high temperature. The reason for the thermal and oxidative instability of the vegetable-based rolling oils is the double bond in the fatty acid.

Conclusions

FTIR Spectroscopy using Horizontal Attenuated Total Reflectance provided useful information on the percentage of cis and trans isomers in the oil and the extent of thermal oxidation during cold rolling. The methodology developed in this study permitted determination of the percentage of cis/trans components of the unsaturated vegetable- based rolling oils at different temperatures.

The trans isomers observed in the vegetable-based rolling oil were due to rearrangement of the cis isomers of fatty acids. When unsaturated rolling oil is heated, the initial nature of the oil changes significantly. The decrease in cis configuration with increase in trans is evidence of transformation that occurs in the unsaturated fatty acids, which the oil initially contains. The rearrangement causes a decrease in the oil's performance capacity. Determination of unsaturation in rolling oils allows their classification and evaluation of their oxidative deterioration, which can be related directly to the unsaturated fatty acids. The results obtained here can be used to predict the state of oxidation in rolling oils.

Acknowledgments

The Authors express their gratitude to ISCOR Technology division for supplying us with rolling oils. PJ Mogwaneng thanks IMMRI for the use of their instrument. Financial support from the University of Pretoria and the NRF, Pretoria, is gratefully acknowledged.

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Figure 1

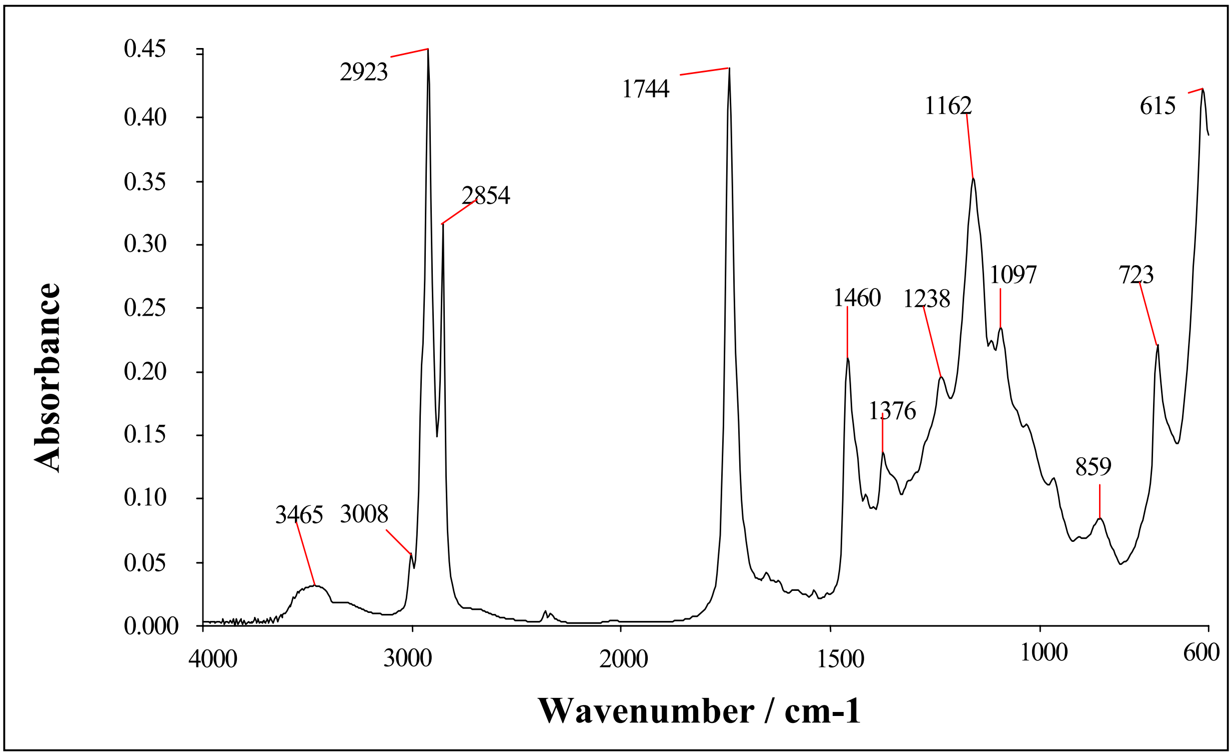


Figure 2

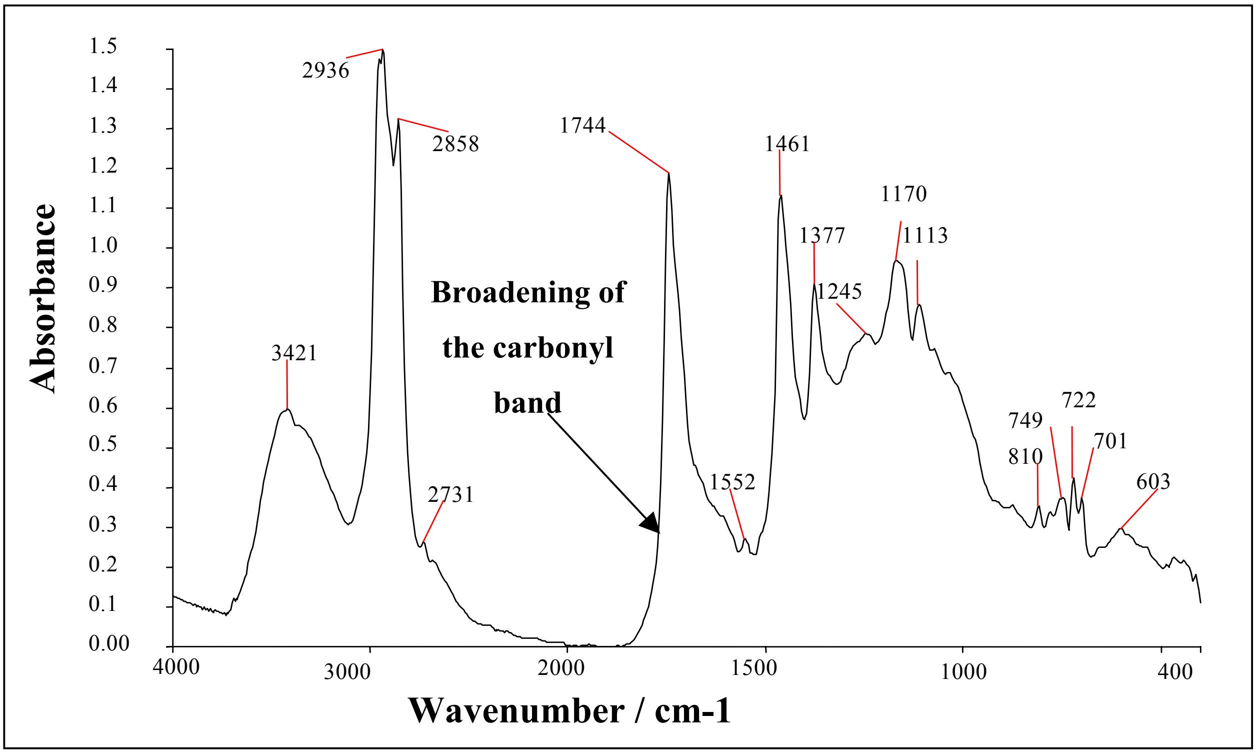


Figure 3

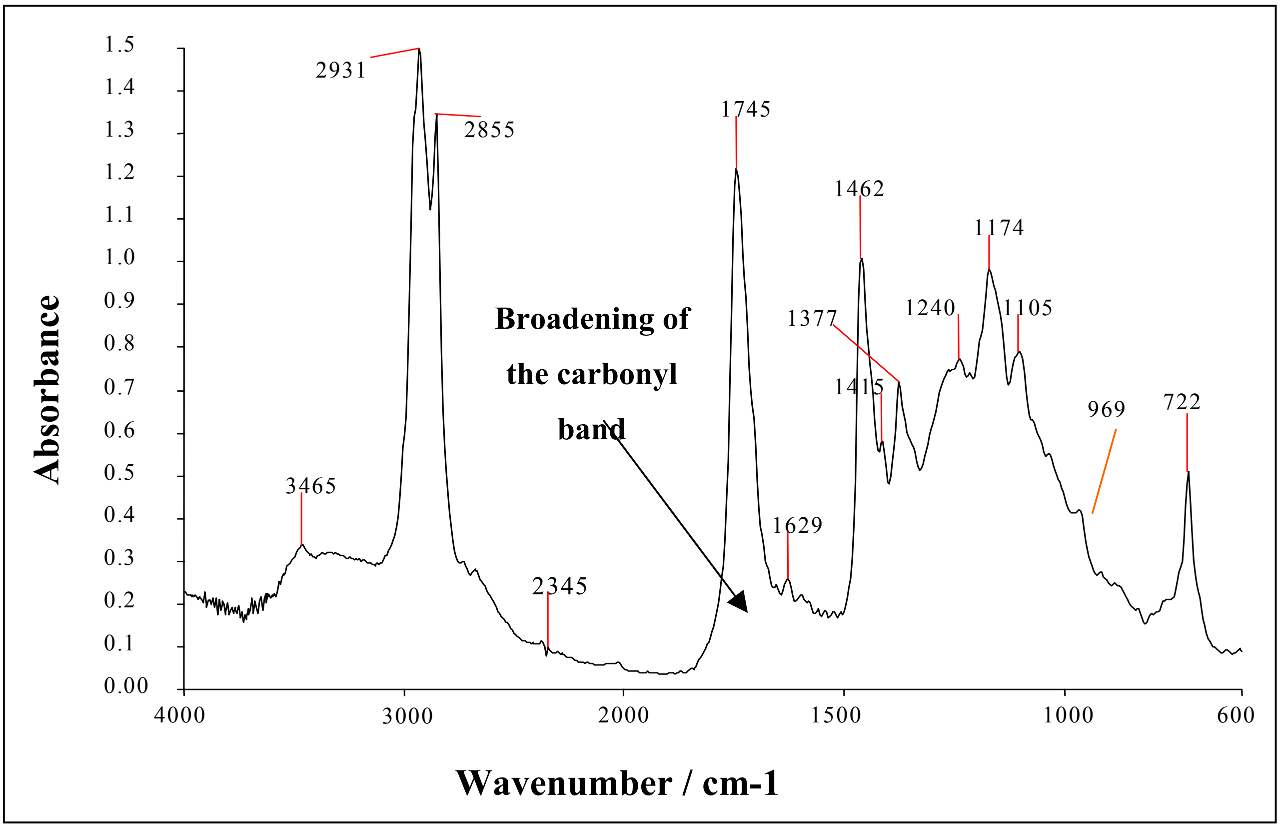

2931
2855
1745
1462
1174
1377
1240
1105
1415
969
722
3465
1629
2345
Broadening of the carbonyl band
Absorbance
1.5
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.00
4000
3000
2000
1500
1000
600
Wavenumber / cm-1

Figure 4

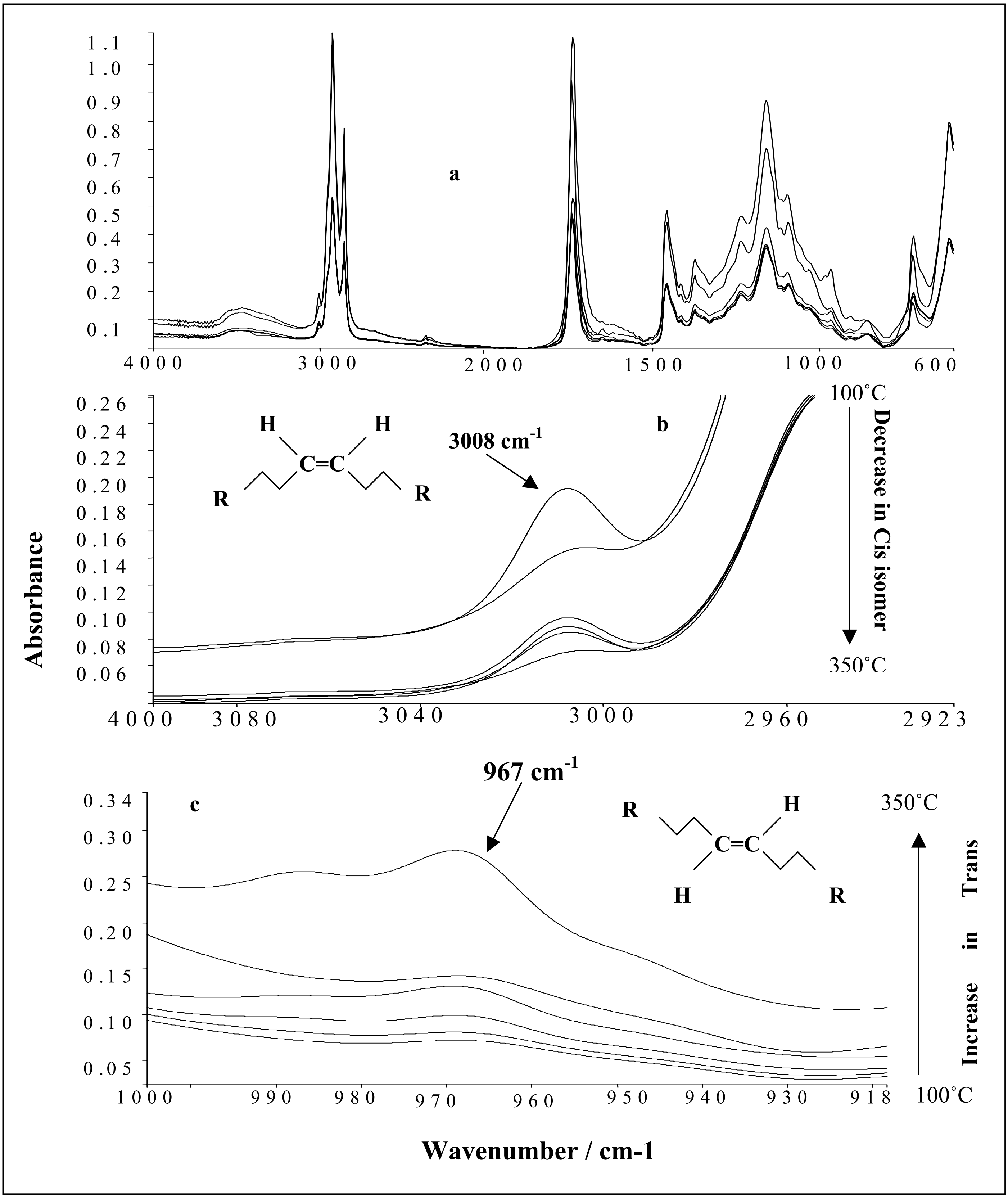

1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
a
4000
3000
2000
1500
1000
600
0.26
0.24
0.22
0.20
0.18
0.16
0.14
0.12
0.10
0.08
0.06
H
H
C=C
R
R
3008 cm-1
b
100°C
Decrease in Cis isomer
350°C
4000
3080
3040
3000
2960
2923
Absorbance
967 cm-1
0.34
0.30
0.25
0.20
0.15
0.10
0.05
c
R
H
C=C
H
R
350°C
Increase in Trans
100°C
1000
990
980
970
960
950
940
930
918
Wavenumber / cm-1

Figure 5

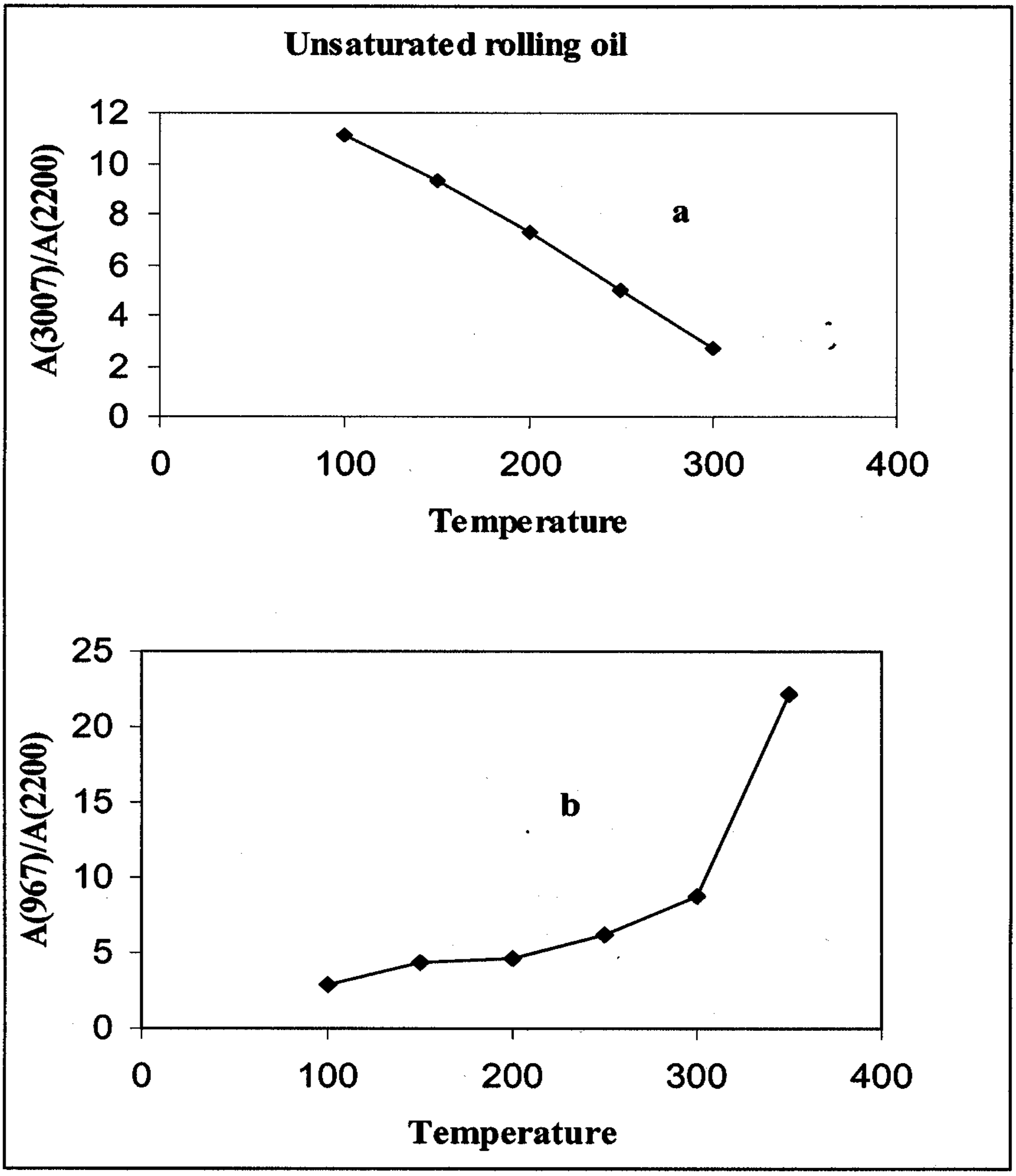

Unsaturated rolling oil
A(3007)/A(2200)
12
10
8
6
4
2
0
0
100
200
300
400
Temperature
a
A(967)/A(2200)
25
20
15
10
5
0
0
100
200
300
400
Temperature
b

Figure 6

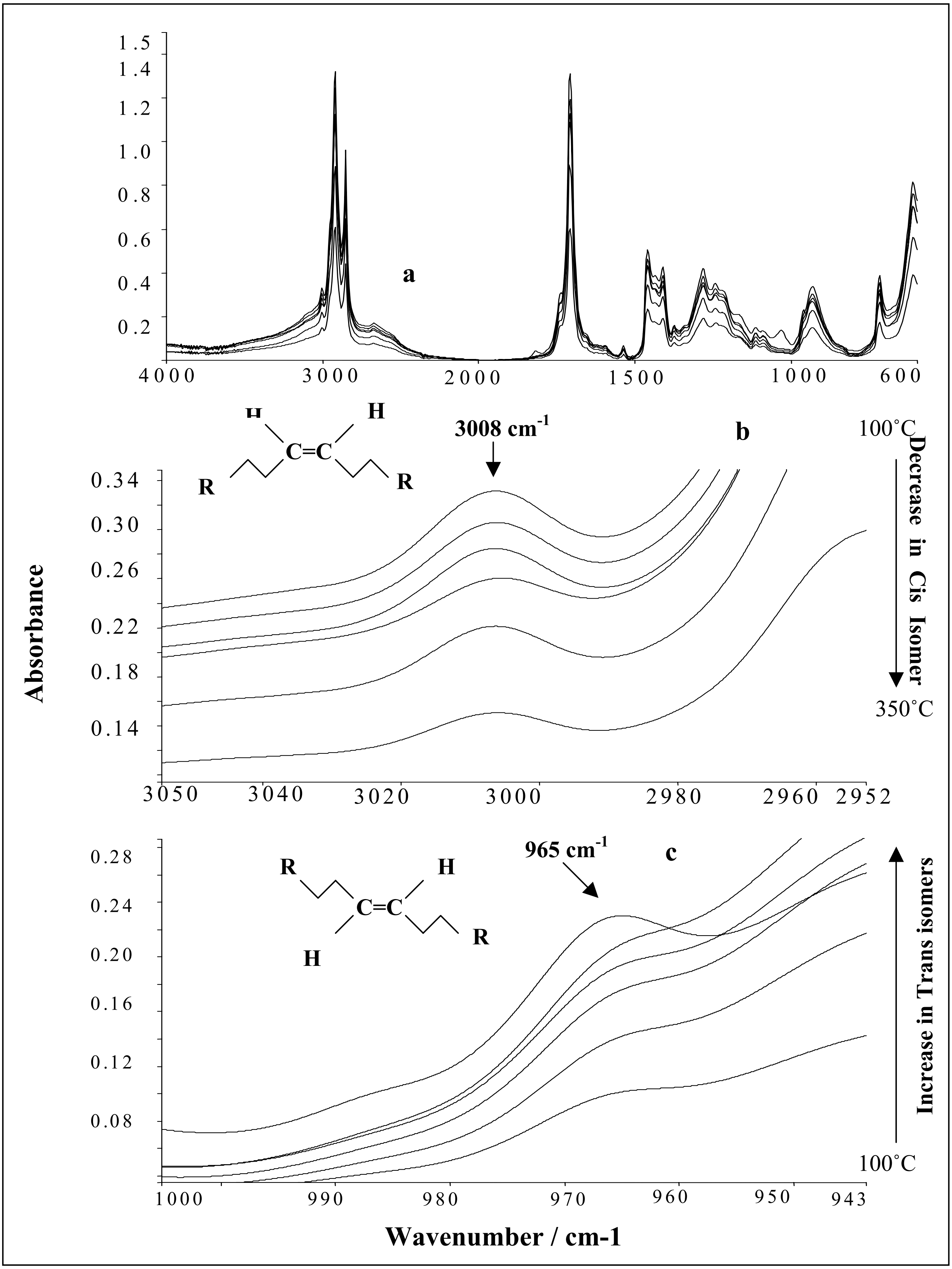

1.5
1.4
1.2
1.0
0.8
0.6
0.4
0.2
a
4000
3000
2000
1500
1000
600
H
H
C=C
R
R
3008 cm-1
b
100˚C
Decrease in Cis Isomer
350˚C
0.34
0.30
0.26
0.22
0.18
0.14
3050
3040
3020
3000
2980
2960
2952
Absorbance
0.28
0.24
0.20
0.16
0.12
0.08
R
H
C=C
H
R
965 cm-1
c
Increase in Trans isomers
100˚C
1000
990
980
970
960
950
943
Wavenumber / cm-1

Figure 7

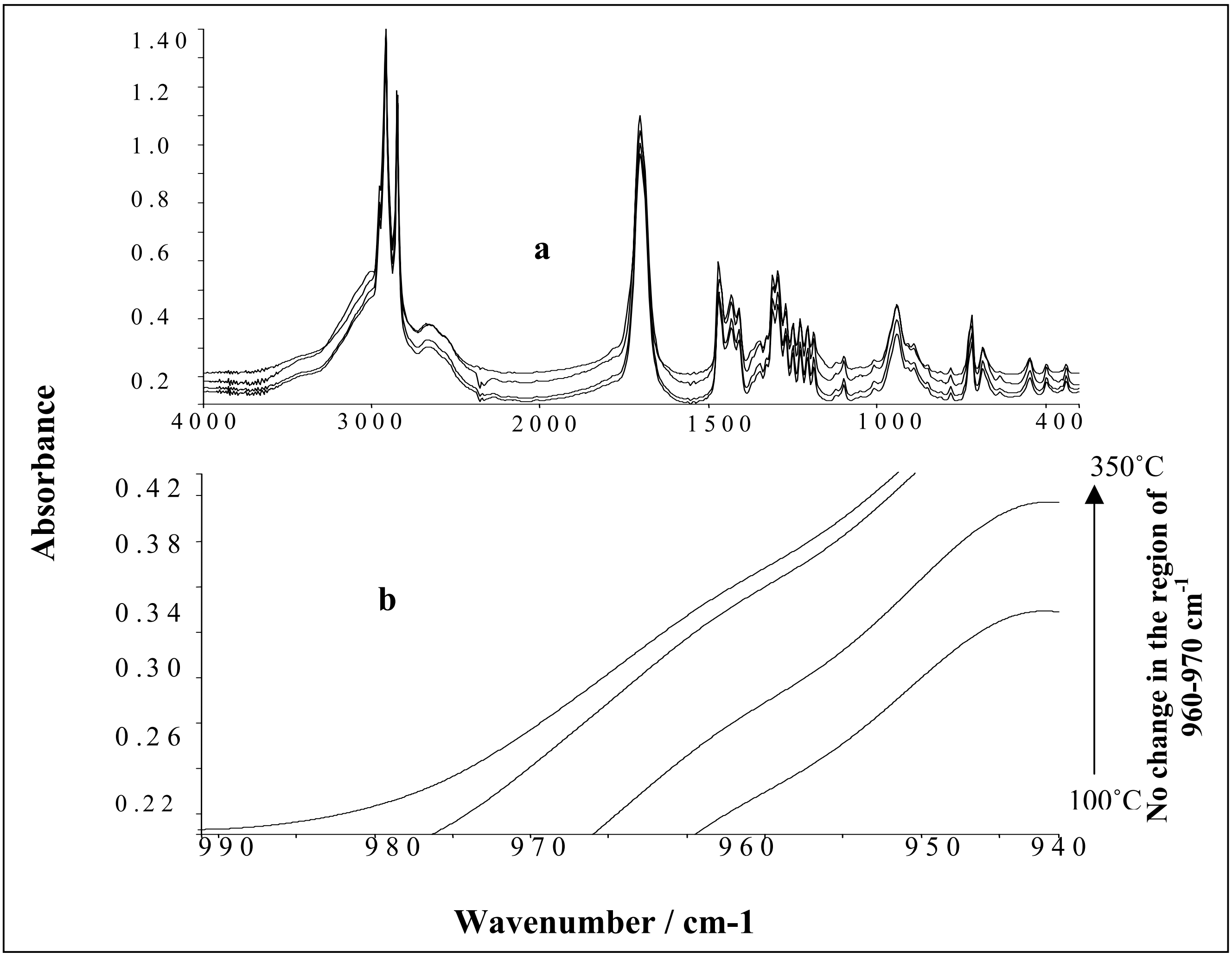

Absorbance
1.40
1.2
1.0
0.8
0.6
0.4
0.2
a
4000
3000
2000
1500
1000
400
0.42
0.38
0.34
0.30
0.26
0.22
b
990
980
970
960
950
940
350˚C
100˚C
No change in the region of 960-970 cm-1
Wavenumber / cm-1

Figure captions

Figure 1: Infrared spectrum of neat vegetable-based rolling oil.

Figure 2: Infrared spectrum of the vegetable-based rolling oil residues left of the steel surface after rolling process.

Figure 3: Infrared spectrum of the thermally oxidized vegetable-based rolling oil heated to ≈400˚C.

Figure 4: Infrared spectra of a vegetable based rolling oil.

a - Infrared spectra of a vegetable based rolling oil previously heated to 100˚C, 150˚C, 200˚C, 250˚C, 300˚C and 350˚C (from top to bottom).

b - Infrared spectra showing the band used to determine unsaturation (3008 cm-1) this band is due to the stretching of the C-H bond adjoining the double C=C bond.

c - Infrared spectra showing the band (968 cm-1) of isolated C=C double bond with trans configuration.

Figure 5: The calibration line of the vegetable based rolling oil.

a - The graph showing decrease in unsaturation (3007 cm-1) with an increase in temperature.

b - The graph showing an increase in trans isomer (967 cm-1) with increase in temperature.

Figure 6: Infrared spectra of oleic acid – example of an unsaturated compound.

- **a -** Infrared spectra of Oleic acid previously heated to 100˚C, 150˚C, 200˚C, 250˚C, 300˚C and 350˚C (From top to bottom).
- **b -** Infrared spectra showing the band used to determine unsaturation (3008 cm-1). This band is due to the stretching vibration of the C-H bond adjoining the double C=C bond.
- **c -** Infrared spectra of the band (965 cm-1) of isolated double C=C bond with trans configuration.

Figure 7: Infrared spectra of Palmitic acid – example of a saturated compound.

- **a -** Infrared spectra of Palmitic acid previously heated to 100˚C, 150˚C, 200˚C and 250˚C (from bottom to top).
- **b -** Infrared spectra of Palmitic acid showing no change at 965 cm-1.

Appendix 1

Table I

Traditional Rolling oil tests.

Test	Description
Oil concentration	Oil concentration in water emulsion
Saponification value	Amount of -COO- groups (including -COOH) per unit weight of rolling oil(according to ASTM D94)
Acid value	Amount of -COOH groups per unit mass of rolling oil(according to ASTM D974)
Residual carbon	Contamination control of rolling oil (index of strip cleanliness)
ESI	Emulsion stability index
SI	Spreading index
BOI	Burn-off index
Ph	pH of emulsion
Viscosity	Viscosity of undiluted oil (according to ASTM D445, 40°C)
Density	According to ASTM D1217, 40°C
Falex test	Failure load [p.s.i. At 40°C]
Chloride test	According to ASTM D1317
Sulphur test	According to ASTM D1552
Flash point	According to ASTM D93

Table II

Bands assignment of a neat vegetable based oil.

Wavenumber (cm-1)	Assignment
3465	O-H stretch
3044-3008	C-H terminal stretch of C=C
2970-2950	C-H stretch of CH3
2865-2845	C-H stretch of CH2
1750-1730	C=O stretch of an ester
1711-1700	COOH of an acid
1460	C-H bend of CH3
1376	C-H bend of CH3
1200-900	Fingerprinting region
723	C-H rocking

Table III

Total height of the cis configuration of the unsaturation (3007 cm-1) band with an increase in temperature.

Temperature (°C)	**Total height (3007 cm-1)**	**Total height (2200 cm-1)**	**A (3007)/ A (2200)**
100	0.1849	0.0167	11.07
150	0.1809	0.0194	9.32
200	0.1768	0.0243	7.28
250	0.1251	0.0252	4.96
300	0.0492	0.0183	2.69
350	0.07	0.005	14.00

Table IV

Total height of the trans configuration of the unsaturation (967 cm-1) with an increase in temperature.

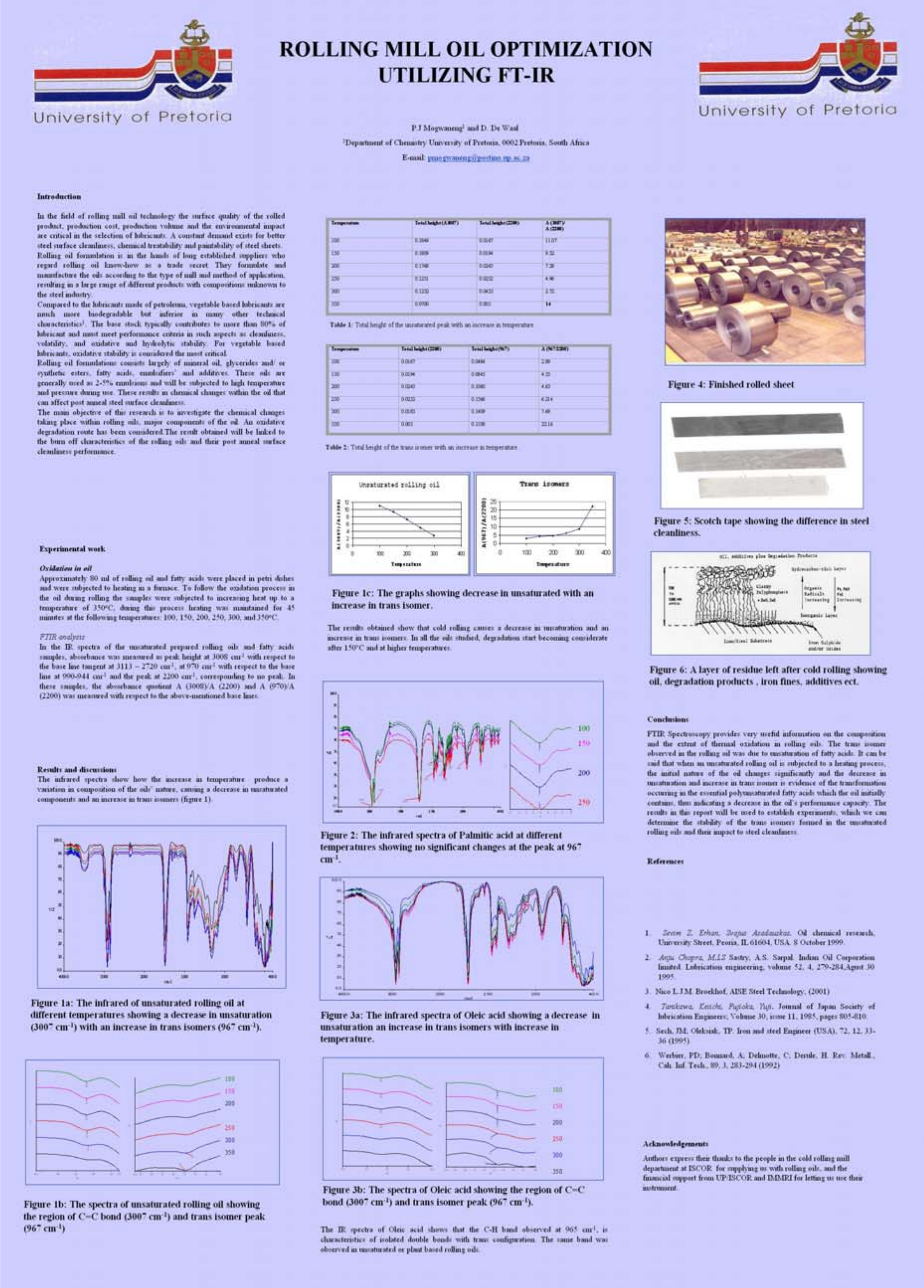
Temperature (°C)	Total height (2200 cm-1)	Total height (967 cm-1)	A (967)/ A (2200)
100	0.0167	0.0484	2.89
150	0.0194	0.0845	4.35
200	0.0243	0.106	4.63
250	0.0252	0.1566	6.21
300	0.0183	0.1409	7.69
350	0.005	0.1108	22.16

- Appendix B -

Contribution to the conference
INORGANIC 2003
Inorganic Chemistry Division of the
South African Chemical Institute (SACI)

Held at
ROODE VALLEI COUNTRY LODGE
Pretoria
08-11 June 2003

Appendix B



University of Pretoria

ROLLING MILL OIL OPTIMIZATION UTILIZING FT-IR

P.J Mogwaneng[1] and D. De Waal
[1]Department of Chemistry University of Pretoria, 0002 Pretoria, South Africa
E-mail: pmogwaneng@postino.up.ac.za

Introduction

In the field of rolling mill oil technology the surface quality of the rolled product, production cost, production volume and the environmental impact are critical in the selection of lubricants. A constant demand exists for better steel surface cleanliness, chemical treatability and paintability of steel sheets.

Rolling oil formulation is in the hands of long established suppliers who regard rolling oil know-how as a trade secret. They formulate and manufacture the oils according to the type of mill and method of application, resulting in a large range of different products with compositions unknown to the steel industry.

Compared to the lubricants made of petroleum, vegetable based lubricants are much more biodegradable but inferior in many other technical characteristics[1]. The base stock typically contributes to more than 80% of lubricant and must meet performance criteria in such aspects as cleanliness, volatility, and oxidative and hydrolytic stability. For vegetable based lubricants, oxidative stability is considered the most critical.

Rolling oil formulations consists largely of mineral oil, glycerides and/ or synthetic esters, fatty acids, emulsifiers' and additives. These oils are generally used as 2-5% emulsions and will be subjected to high temperature and pressure during use. These results in chemical changes within the oil that can affect post anneal steel surface cleanliness.

The main objective of this research is to investigate the chemical changes taking place within rolling oils, major components of the oil. An oxidative degradation route has been considered.The result obtained will be linked to the burn off characteristics of the rolling oils and their post anneal surface cleanliness performance.

Experimental work

Oxidation in oil

Approximately 80 ml of rolling oil and fatty acids were placed in petri dishes and were subjected to heating in a furnace. To follow the oxidation process in the oil during rolling the samples were subjected to increasing heat up to a temperature of 350°C, during this process heating was maintained for 45 minutes at the following temperatures: 100, 150, 200, 250, 300, and 350°C.

FTIR analysis

In the IR spectra of the unsaturated prepared rolling oils and fatty acids samples, absorbance was measured as peak height at 3008 cm^{-1} with respect to the base line tangent at 3113 – 2720 cm^{-1}, at 970 cm^{-1} with respect to the base line at 990-944 cm^{-1} and the peak at 2200 cm^{-1}, corresponding to no peak. In these samples, the absorbance quotient A (3008)/A (2200) and A (970)/A (2200) was measured with respect to the above-mentioned base lines.

Results and discussions

The infrared spectra show how the increase in temperature produce a variation in composition of the oils' nature, causing a decrease in unsaturated components and an increase in trans isomers (figure 1).

Figure 1a: The infrared of unsaturated rolling oil at different temperatures showing a decrease in unsaturation (3007 cm^{-1}) with an increase in trans isomers (967 cm^{-1}).

Figure 1b: The spectra of unsaturated rolling oil showing the region of C=C bond (3007 cm^{-1}) and trans isomer peak (967 cm^{-1})

Temperature	Total height (A3007)	Total height (2200)	A (3007)/ A (2200)
100	0.1649	0.0147	11.07
150	0.1806	0.0194	9.32
200	0.1768	0.0243	7.28
250	0.1251	0.0252	4.96
300	0.1232	0.0453	2.72
350	0.0700	0.005	14

Table 1: Total height of the unsaturated peak with an increase in temperature

Temperature	Total height (2200)	Total height (967)	A (967/2200)
100	0.0147	0.0464	2.39
150	0.0194	0.0843	4.35
200	0.0243	0.1080	4.45
250	0.0252	0.1566	6.214
300	0.0183	0.1409	7.69
350	0.001	0.2218	22.16

Table 2: Total height of the trans isomer with an increase in temperature

Figure 1c: The graphs showing decrease in unsaturated with an increase in trans isomer.

The results obtained show that cold rolling causes a decrease in unsaturation and an increase in trans isomers. In all the oils studied, degradation start becoming considerate after 150°C and at higher temperatures.

Figure 2: The infrared spectra of Palmitic acid at different temperatures showing no significant changes at the peak at 967 cm^{-1}.

Figure 3a: The infrared spectra of Oleic acid showing a decrease in unsaturation an increase in trans isomers with increase in temperature.

Figure 3b: The spectra of Oleic acid showing the region of C=C bond (3007 cm^{-1}) and trans isomer peak (967 cm^{-1}).

The IR spectra of Oleic acid shows that the C-H band observed at 965 cm^{-1}, is characteristics of isolated double bonds with trans configuration. The same band was observed in unsaturated or plant based rolling oils.

Figure 4: Finished rolled sheet

Figure 5: Scotch tape showing the difference in steel cleanliness.

Figure 6: A layer of residue left after cold rolling showing oil, degradation products , iron fines, additives ect.

Conclusions

FTIR Spectroscopy provides very useful information on the composition and the extent of thermal oxidation in rolling oils. The trans isomer observed in the rolling oil was due to unsaturation of fatty acids. It can be said that when an unsaturated rolling oil is subjected to a heating process, the initial nature of the oil changes significantly and the decrease in unsaturation and increase in trans isomer is evidence of the transformation occurring in the essential polyunsaturated fatty acids which the oil initially contains, thus indicating a decrease in the oil's performance capacity. The results in this report will be used to establish experiments, which we can determine the stability of the trans isomers formed in the unsaturated rolling oils and their impact to steel cleanliness.

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Acknowledgements

Authors express their thanks to the people in the cold rolling mill department at ISCOR for supplying us with rolling oils, and the financial support from UP/ISCOR and IMMRI for letting us use their instrument.