THE DEVELOPMENT OF CREOSOTE (MICRO)EMULSION TO BE USED FOR WOOD PRESERVATION

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THE DEVELOPMENT OF CREOSOTE MACROEMULSIONS TO BE USED FOR WOOD PRESERVATION

BY

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Declaration

I the undersigned hereby declare that the work contained in this dissertation is my own original work and has not previously in its entirety or in part been submitted at any university for a degree.

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17/9/1998

Date

Abstract

Creosote treated timber "bleeds" profusely in hot weather and develops tarry, oily surfaces that are difficult to handle and pose a health hazard. The objective of this work is to investigate the possibility of improving the surface condition of the creosote treated timber. The possibility of using creosote macroemulsions for wood impregnation purposes was investigated. Creosote emulsions also present the possibility of improving other creosote characteristics such as penetration and distribution of creosote in wood during treatment.

Creosote emulsions were successfully developed by identifying the suitable class of surfactants (anionic), chemical type of surfactant (unsaturated fatty acids), and type of emulsion (water-in-oil). However, these emulsions could not improve the surface condition of the creosote treated timber. The penetration and distribution characteristics of both the creosote emulsion and unemulsified creosote were satisfactory. Both the creosote emulsion and the unemulsified creosote penetrated the sapwood completely but there was no penetration into the hardwood.

In memory of my father

Bernard Sithembiso "Matewu" Nzimande

(1950 - 1998)

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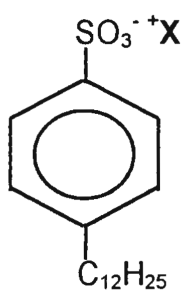
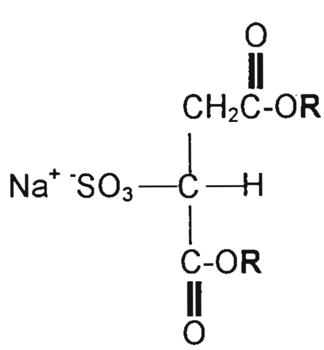
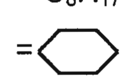
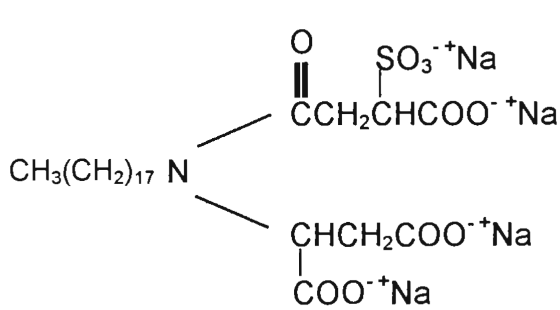
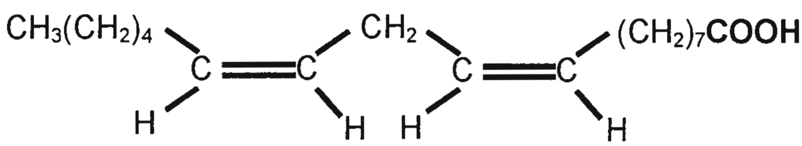
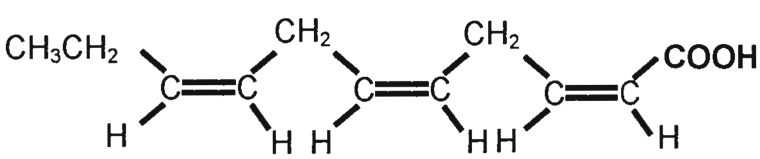
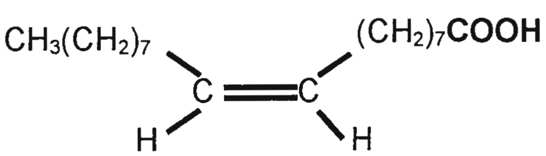
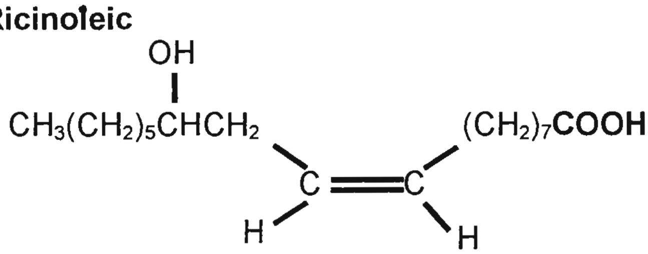
A Abbreviations

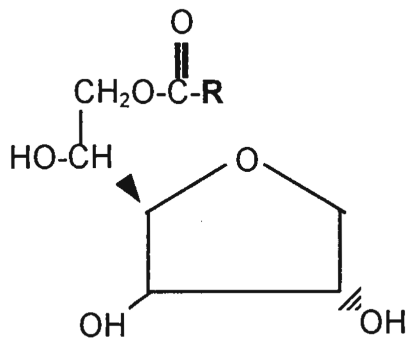
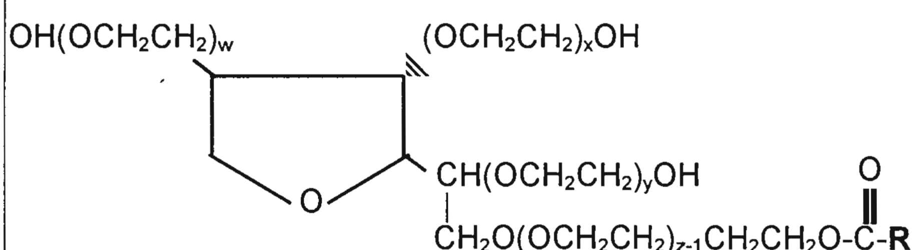
Symbol	Definition
A_v	acid value
APM	alternating pressure method
ADSD	average droplet size distribution
CMC	critical micelle concentration
CTO	crude tall oil
Dys	days
C	emulsion concentration
HLB	hydrophile-lipophile balance
A	interfacial area between bulk liquids
MC	medium creosote
Min	minutes
O/W	oil-in-water emulsion
OPM	oscillating pressure method
S	saponification number
SCO	saponified castor oil
B	Span/Tween blend
V	Volume
W/O	Water-in-oil emulsion
E	Weight percentage of oxyethylene
P	Weight percentage of polyhydric alcohol

B Structures, Chemical and Tradenames of Surfactants

Chemical name and structure	Tradename®
Anionic surfactants	
Alkyl aryl sulphonates : dodecyl benzene sulphonates	
 *X* = Na = $(CH_3)_2CHNH_3$ Blend of Nansa YS 94 and coconut diethanolamine	Nansa SS 30 Nansa YS 94 HAC
Sulphosuccinates and Sulphosuccinamates	
 **R** = C_8H_{17}- = 	Aerosol OT-B Aerosol A 196
	Aerosol 22

Chemical name and structure	Tradename®
Anionic surfactants	
Fatty acid soaps (sodium and potassium)	
Linoleic  **Linolenic**  **Oleic**  **Palmitic** $CH_3(CH_2)_{14}$**COOH** **Ricinoleic** 	

Chemical name and structure	Tradename®
Anionic surfactants	
Fatty acid soaps (sodium and potassium)	
Rosin $C_{12}H_{19}$**COOH** (General formula) : Resin acid with penantrene nucleus **Stearic** $CH_3(CH_2)_{16}$**COOH** **Castor oil** Triglycerides of Stearic 0.3 Oleic 8.0 Linoleic 3.6 Ricinoleic 87.8 **Crude tall oil** Rosin 32 Oleic 28 Linoleic 18 Linolenic 2 Palmitic 2 Stearic 1 Other acids and unsaponifiable matter 17 **Linseed oil** Triglycerides of Oleic 5.0 Linoleic 61.5 Linolenic 25.0 Palmitic 5.0 Stearic 3.5 **R30-5** Rosin 30 Oleic 30 Linoleic 28 Linolenic 4 Palmitic 1 Stearic 2 Unsaponifiable matter 5	

Chemical name and structure	Tradename®
Nonionic surfactants	
Sorbitan esters	
	
R	
= monolauric [$CH_3(CH_2)_{10}$ -]	Span 20
= monopalmitic	Span 40
= monostearic	Span 60
= monooleic	Span 80
tristearic	Span 65
trioleic	Span 85
Polyoxyethylene sorbitan esters	
	Tween 20 To Tween 85 as for Span above
$w + x + y + z = 20$	
R as for sorbitan esters above	
Oxoalcohol ethoxylates	
C_{12} - C_{13} : $(-OCH_2CH_2)_3$ referred to as AM 13	
C_{12} - C_{13} : $(-OCH_2CH_2)_7$ referred to as AM 14	

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1 INTRODUCTION

Coal tar creosote has been in use as a wood preservative throughout the world for over 150 years (Loiseau, 1994; Pommer, 1996). It has been used in fabric preservation and also in the fields of medicine, pharmacy, dyes, chemicals, carbon blacks and fuels (Pizzi *et al.*, 1984). Creosote is a brownish-black, oily liquid produced by fractional distillation from coal tar within the distillation range of 200-400 ^{0}C (BSI 1282, 1975; Loiseau, 1994; Pommer, 1996). The main components of creosote are polyaromatic hydrocarbons (PAH's). Other components include tar acids (e.g. phenols, cresols and other cresylic acids) and tar bases (e.g. pyridines, quinolines and acridines) (Brink, 1983; Mueller *et al.*, 1989; Loiseau, 1994; Pommer, 1996).

In South Africa, there are two main suppliers of coal tar creosote viz., Sasol Carbo-Tar (PO Box 4590, Johannesburg, 2000, South Africa) and Suprachem (PO Box 98048, Wepark, 0146, South Africa) (Pizzi *et al.*, 1984). The creosote produced by Sasol Carbo-Tar is a by-product of the medium temperature coal gasification process (Nowacki, 1979; Mangold *et al.*, 1982; Brink, 1983). The creosote produced by Suprachem is derived from the high temperature coking of bituminous coal for steel production.

The advantages of using creosote as a wood preservative are that it is relatively inexpensive, almost insoluble in water and does not cause deterioration of timber strength on treatment (Loiseau, 1994). Other attributes are that it is not corrosive to metals, it protects timber against splitting and weathering (BSI 1282, 1975), it has a high electrical resistance and is available in several grades to suite different applications (BS 144, 1997).

The diverse and colourful history of creosote preservatives has been marred mainly by inherent problems of odour, skin irritation and related product handling problems (Nowacki, 1979; Loiseau, 1994). Other problems associated with the utilization of creosote include flammability, pollution (Mueller *et al.*, 1989) and the development of oily, dirty surfaces termed "crud" of the creosote treated wood.

Over the years, complaints on the handling difficulties and odour associated with creosote treated products have been widespread (Mueller *et al.*, 1989; Watkins *et al.*, 1992). Creosote treated timber "bleed' profusely in hot weather and develop crud (Watkins *et al.*, 1992). Such surfaces are difficult to handle and they pose health hazards (Brink, 1983). Some or all of the above limit the use of creosote to the treatment of timber which is unlikely to come into contact with people or livestock. In order to sustain the competitiveness of creosote in the wood preservation market, the problems of the surface condition of creosote treated poles should be eliminated.

The aim of this project is to improve the surface condition of creosote treated timber using creosote emulsions. Creosote emulsions also present the possibility of improving other characteristics of creosote such as penetration and distribution in the treated wood. This study focused on the identification of a suitable surfactant and a suitable process for the successful emulsification of creosote to be used for wood impregnation purposes.

This study is divided into the following sections;

(i) Identification of a suitable surfactant for creosote emulsion
(ii) Identification of the most suitable emulsion formulation
(iii) Identification of the most suitable type of emulsion (water-in-oil (W/O) vs oil-in-water (O/W))

(a) Wood impregnation tests with creosote emulsions (laboratory scale)

(b) Wood impregnation tests with creosote emulsions (pilot scale)

The following chapters focus on the theoretical background of wood preservatives, the preparation and properties of emulsions and the experimental work done on the preparation of creosote emulsions and wood impregnation tests. Thereafter the results are discussed and a conclusion on the suitability of creosote emulsions for wood preservation is drawn.

2 LITERATURE SURVEY

Emulsion and Wood Preservation

The first section of this chapter gives a theoretical background to the process of emulsification in general. The second section deals with wood preservatives and different wood treatment processes.

2.1 EMULSION

2.1.1 Introduction

A wide range of industrial and commercial emulsions are formulated to suite various physical, chemical, and biological requirements. With such diverse applications, it is not surprising that the techniques of emulsification have developed largely on trial-and-error experience. A good deal of physico-chemical information is now available on the process of emulsion formation. By necessity, the basic knowledge refers to rather idealized situations and simple systems.

2.1.2 Theory of emulsion

Emulsions are dispersed, multiphase systems consisting of two or more almost mutually insoluble liquids, with the dispersed (internal) phase present in the form of droplets in a continuous (external) phase. There are generally two types of emulsions, viz., oil-in-water (O/W) and water-in-oil (W/O) emulsions according to the nature of the internal phase. All emulsions have at least one polar hydrophilic liquid and one lipophilic liquid.

The diameter of the droplet size in the internal phase of macroemulsions lies between 0.1 μ and 0.1 mm, usually there is broad size distribution. Emulsions with the ratio between the smallest and the largest droplet size of 1:10 are thermodynamically unstable, i.e., the droplets tend to coalescence due to the reduction in the phase interface. Microemulsions are thermodynamically stable and typically have droplet diameters smaller than the wavelength of visible light, lying in the range of 10 to 300 nm (Mittal, 1977a; Gillberg *et al.*, 1978; Huang, 1989; Brun and Wade, 1990; Greiner and Evans, 1990; Farago *et al.*, 1990; Ogino and Abe, 1993).

Since the macroemulsions are systems of at least two phases, energy may be added in the form of mechanical energy or chemical energy, which later causes "spontaneous" emulsification.

2.1.3 Emulsion stability

Emulsion stability has been the subject of many detailed studies (Kitchener and Mussellwhite, 1968; Boyd *et al.*, 1972; Friberg and Gillberg-La Force, 1975; Chieu *et al.*, 1977; Hazlett and Schechter, 1988; Goubran and Garti, 1988; Sax *et al.*, 1988; Ruckenstein *et al.*, 1989; Zapol'skii *et al.*, 1989; Cavallo and Chang, 1990; Chen and Ruckenstein, 1990; Graillat *et al.*, 1990; Kizling and Kronberg, 1990; Saito *et al.*, 1990; Williams *et al.*, 1990; Avranas *et al.*, 1991;Ciullo and Bruan, 1991; Williams, 1991; Wojdak *et al.*, 1991;Bibette, *et al.*, 1992; Kim and Wasan, 1996; Kumar *et al.*, 1996; Yan and Masliyah, 1997).

Macroemulsions are thermodynamically unstable and they are subject to change over time. The dispersed droplets will coalesce and phase separate.

Two types of instabilities are commonly associated with an emulsion;

- *flocculation* (Borwankar *et al.*, 1992) - a reversible aggregation of the dispersed-phase droplets that eventually separate in a gravitational field (called creaming) with the droplets retaining their integrity,

- *coalescence* (Borwankar *et al.*, 1992) - an irreversible fusion of droplets that reduces the interfacial area and therefore, the interfacial free energy of the system. As a result, the emulsion separates into discrete bulk phases. The coalescence process can be divided into three separate stages. First, two droplets must collide (usually due to Brownian motion or externally applied fields) bringing two droplets into contact. The second stage is the thinning of the film separating the two droplets followed by the sudden merging of the two droplets.

2.1.3.1 Determination of emulsion stability

A further consideration in any discussion of instability of emulsions is the time scale and conditions of treatment concerned. Although it is not possible to express emulsion stability by a simple number applicable to all circumstances, it is evident that the rates of degradation of different types of emulsion vary enormously.

In the past, many tests have been developed to determine emulsion stability (Sax *et al.*, 1988; Hazlett and Schechter, 1988; Cavallo and Chang, 1990). These tests were based on droplet coalescence rates. Viscosity measurements can also provide indications of emulsion stability. Changes in a system's viscosity indicate droplet coalescence and phase separation. In W/O emulsion systems, droplet interaction can be investigated by measuring the electrical conductivity. An increase in conductivity indicates droplet aggregation, which can lead to phase separation.

All of the methods discussed above, however, require time and multiple measurements over time in order to get accurate information on the stability of an emulsion.

2.1.3.2 Enhancing emulsion stability

2.1.3.2.1 Surfactant concentration

Surfactants are surface-active agents consisting of both hydrophilic and lipophilic groups. Since surfactants mainly act in aqueous systems, they are classified according to the chemical structure of their hydrophilic groups. The hydrophilic groups may be ionic or nonionic and their chemical structure can vary widely. Surfactants can be divided into four different classes, viz., anionics (Linfield, 1976a and 1976b), nonionics (Schick, 1965; Becher and Trifiletti, 1973), cationics (Jungermann, 1970) and amphoterics.

Anionics and cationics are amphiphilic compounds in which the hydrophilic residues carry anionic and cationic groups respectively with counterions. Nonionics do not dissociate into ions in aqueous solution. Amphoterics have zwitterionic hydrophilic groups. The examples of different classes of surfactants are given in Table 2.1.4a.

Table 2.1.4a

Examples of different classes of surfactants (Jungermann, 1970; Porter, 1994)

Class of surfactant	Example
Anionic	$C_{12}H_{25}CO\text{-}O^{-}Na^{+}$
Cationic	$C_{12}H_{25}N(CH_3)_3^{+}Cl^{-}$
Nonionic	$C_{12}H_{25}\text{-}O\text{-}(CH_2CH_2O)_7\text{-}H$
Amphoteric	$C_{12}H_{25}N^{+}(CH_3)_2\text{-}CH_2COO^{-}$

Surfactants form an interfacial film around the dispersed-phase droplets that prevents or retards droplet coalescence and flocculation. A sufficient quantity of surfactant must be present in a formulation to cover all of the newly created interfacial surfaces that result from dispersion. Emulsion instabilities are, however, sensitive to the concentration of a surfactant, particularly a nonionic surfactant. A critical surfactant concentration exists above which the breakdown of the emulsion (through flocculation or coalescence) occurs at an accelerated rate.

2.1.3.2.2 Critical micelle concentration

The minimum amount of a surfactant needed for a particular system can be obtained by determining the critical micelle concentration (CMC) (Schwartz *et al.*, 1958; Shinoda, 1967, Mittal, 1977b; Cavallo and Chang, 1990), the concentration at which a minimum is obtained in the log C vs γ plot, where C is the concentration of a surfactant and γ is the surface tension. Beyond this critical concentration, the surface tension will not be reduced further when the surfactant is added. As the surfactant is added to water, it solubilizes and disperses. As more surfactant is added, a dynamic equilibrium is established between the loosely formed aggregates (micelles) and the solubilized surfactant. This equilibrium continues until the system is completely saturated with the surfactant, at which point micelles become the major species in solution. Commercial emulsions generally contain a large excess of surfactants. Very often, a reduction in the amount of the surfactant used compromises the stability of the system.

2.1.4 Selection of a surfactant

When an emulsion has to be made, there is a very wide choice of surfactants. Out of this welter of products, comes the task of selecting one or two products that will satisfactorily emulsify the chosen ingredients. Griffin (1949, 1954) introduced a semi-empirical procedure for selecting an appropriate surfactant, or a blend of surfactants, to prepare an emulsion.

This procedure is based on the concept called "Hydrophile-Lipophile Balance" (HLB) (Shinoda and Sagitani, 1977; Shinoda, 1978; Graillat *et al.*, 1990). The essential feature of a surfactant is that it has affinities for both the aqueous and the organic phases. When the surfactant molecule is adsorbed at the interface between the aqueous and the organic phases, these affinities can be satisfied simultaneously. This is achieved by the orientation of its hydrophilic portions towards the aqueous phase and its lipophilic portions towards the organic phase. The ratio of the weight percentages of the hydrophilic and lipophilic portions should therefore influence emulsification behaviour of the surfactant.

Although earlier workers (Reychler, 1913) had suggested this idea of "balance", special attention was focused on it by Epstein and Harris (1933). In the late 1940's, Atlas Powder company (Griffin, 1949) applied it in a system for selecting surfactants for specific applications. An empirical number has been assigned to each surfactant in the Atlas range, representing its HLB; the lower the HLB number, the more lipophilic is the material and the higher the HLB number, the more hydrophilic is the material. The choice of a suitable surfactant for a specific emulsion may then be narrowed down by reference to tables (Appendix I) which have been compiled showing the "required HLB" for emulsification of a wide range of commonly used organic compounds. It is emphasized that whereas the type of emulsion promoted is a function of HLB, the efficiency of a surfactant of the required HLB depends on the chemical nature of the surfactant.

Originally the most suitable surfactant, or blend of surfactants, was determined by a tedious process of "trial-and-error". In the late 1960's, several methods had been proposed to determine the HLB values of nonionic surfactants and oils, so that a simple calculation indicates what surfactant blend should be employed. Approximate HLB values for polyhydric fatty acid esters can be calculated from analytical data,

$$HLB = 20(1 - S/A_V) \quad \text{....................1 (Sherman, 1968)}$$

where S is the saponification number of the ester, and A_V is the acid value of the fatty acid residue. In certain cases, it is difficult to determine saponification numbers accurately e.g., esters of tall oil. A relationship based on composition is used for these cases,

$$HLB = (E + P)/5 \quad \text{.......................2 (Sherman, 1968)}$$

where E is the weight percentage of oxyethylene, and P is the weight percentage of polyhydric alcohol. When the only hydrophilic group present is ethylene oxide, and also for ethylene oxide derivatives, this reduces to,

$$HLB = E/5 \quad ....3$$

Ionisation of the hydrophilic group in ionic materials tend to make them even more hydrophilic in character, so that their HLB values cannot be determined on a weight percentage basis. The influence of the HLB of the surfactant on its performance is given in Table 2.1.4b.

Table 2.1.4b

Influence of HLB on performance (ICI, 1984;Sherman, 1968)

HLB range	Dipersibility in water	Suitable application
1-4	Nil	-
3-6	Poor	W/O emulsifier
6-8	Milky dispersion on agitation	Wetting agent
8-10	Stable milky dispersion	Wetting agent *O/W emulsifier*
10-13	Translucent to clear dispersion	O/W emulsifier
13	Clear solution	O/W emulsifier *Solubilizing agent*

2.1.5 Mode of adding the surfactant

Having chosen the appropriate surfactant, there are four recognized ways of incorporating the surfactant into the system, viz., surfactant-in-water method, surfactant-in-oil method, nascent soap method, and alternate addition method. Surfactant-in-water method is normally used for the preparation of O/W emulsions and the surfactant-in-oil method is suitable for the preparation of W/O emulsions. The nascent soap method is suitable for emulsions that are stabilized by soaps. The nascent soap method depends upon the *in situ* formation of soap at the interface. In the alternate addition method, water and oil are added alternatively in small portions to the surfactant. In all cases where soaps are employed as surfactants, the nascent soap method is preferred. It results in emulsions with very fine droplets (Dorey, 1946).

In industrial practice, the amount of surfactant used is limited by cost. The minimum amount, which can be used with reasonably satisfactory results, is employed in the formulation of the emulsion. Approximate values of this optimum concentration can be calculated from the CMC discussed in 2.1.3.2.2

2.1.6 Emulsion preparation

Emulsification is a very important process in industry. Numerous machines have been devised with an objective of securing an intimate subdivision of the internal phase in the continuous medium. Generally, droplets of the required size may be obtained by two different approaches. One approach is to start from very tiny nuclei and then allow them to grow to the required size, which is the basic idea of the condensation method. The other approach is to break up large drops of bulk liquid into small droplets, which is the basis of the dispersion method.

A mathematical analysis of the mechanism of the subdivision of one phase into another was made by Rossi (1933), who showed that the state of subdivision is affected mainly by the mechanical action of dispersing one phase into another, and but little by the physico-chemical properties of the emulsion that is already formed. Whilst low interfacial tension facilitates the formation of the emulsion, it has slight effect on the actual stability.

2.1.6.1 Condensation method

This method, developed by Sumner (1933) for application in emulsions, is similar to the standard procedure of growing aerosols (Sinclair and LaMer, 1949; Fuks and Sutugin, 1965). The vapour of one liquid (the dispersed phase), is injected below the surface of another liquid, which forms the external phase of the emulsion. In this process, the vapour becomes supersaturated and condenses as micro-sized droplets. These droplets are stabilized in the external phase, which contains a suitable surfactant.

2.1.6.2 Dispersion method

The common method of preparing emulsions is to apply brute force to break up the interface into fine shreds and globules. There are three broad categories of this method, viz., mixing, colloid milling, and homogenizing. When mixing is applied, the average droplet diameters of the emulsion are usually of the order of 5μ. Droplet diameters of the order of 2μ and 1μ or smaller are easily obtained with colloid mills and homogenizers respectively (Sherman, 1968).

2.1.6.3 Sonic and ultrasonic methods

Other less prominent methods of emulsification include, sonic and ultrasonic methods. Brown and Goodman (1965) pointed out that these methods are supplementary techniques of emulsification which are valuable under certain conditions.

2.1.7 Modes of emulsification and physico-chemical factors

Different modes of emulsification affect different physico-chemical properties of the resultant emulsion (Sumner, 1954; Gopal, 1968; Wilson; 1994).

1994). The modes of emulsification include time of agitation, and the intensity of agitation. The integrity of the formed emulsion depends on physico-chemical factors. These physico-chemical factors include; concentration of emulsion, droplet size, interfacial area, and viscosity. Other physico-chemical properties of importance that are discussed in detail elsewhere in the literature include, oil type, density difference between the two phases, surfactant type and concentration (Becher, 1966; Noro *et al.*, 1979; Amri and Woodburn, 1990; Wilson, 1994). Different modes of emulsification affecting different physico-chemical factors of the resultant emulsions are given in Table 2.1.7.

Table 2.1.7

Modes of emulsification affecting different physico-chemical factors of resultant emulsions (Sherman, 1968)

Mode of emulsification	Physico-chemical factor affected
Time of agitation	1) Emulsion concentration 2) Droplet size
Intensity of agitation	1) Interfacial area

2.1.7.1 Emulsion concentration

Under rather idealized conditions of ultrasonic emulsification, it has been found that the dispersion rate is approximately proportional to the interfacial area A between the bulk liquids and the coagulation rate is proportional to Vc^2, where V is the volume of the emulsion and c is the emulsion concentration. Thus the rate of change of the emulsion concentration (Gopal, 1961) would be given by;

$$\partial(Vc)/\partial t = \alpha A - \beta Vc^2 \quad \text{.......................................} 4$$

where α and β are constants. This requires that the disruption of the bulk interface be the dominant process of dispersion, and the binary collisions among the emulsified droplets be the dominant process of recombination. Equation 4 gives;

$$c = c_\infty \tanh bt\,;\ c_\infty = (A\alpha/\beta V)^{1/2}\,;\ b = (A\alpha\beta/V)^{1/2} \quad ...5$$

The concentration of emulsion increases rapidly at first and soon reaches a limiting value c_∞. (Fig. 2.1.7.1).

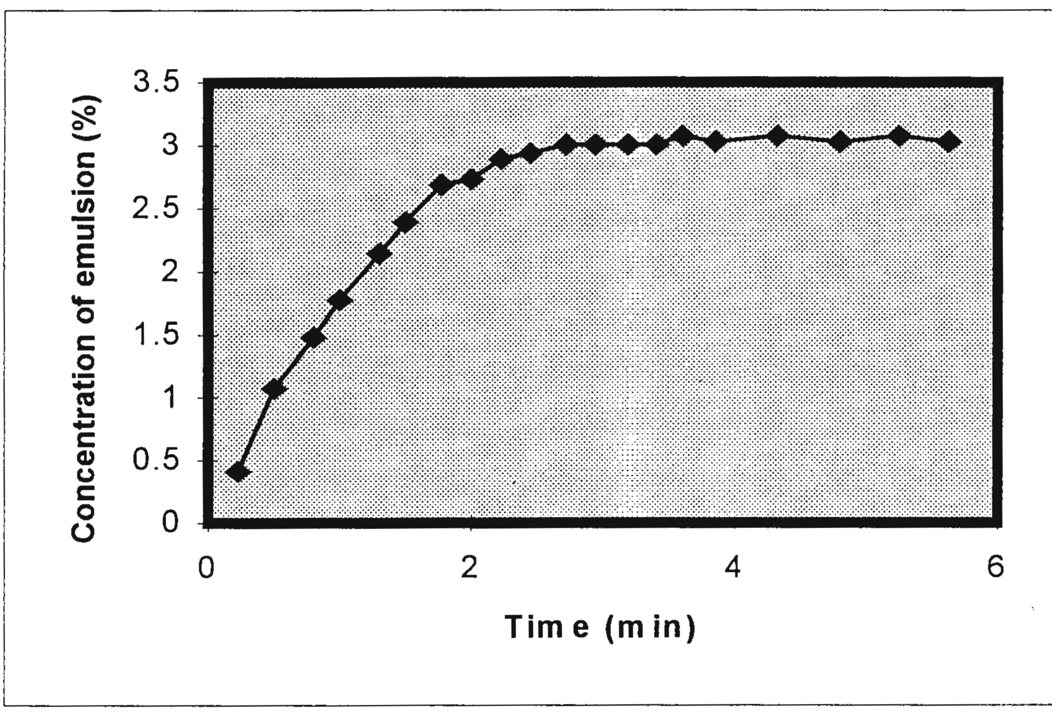


Figure 2.1.7.1: Growth of emulsion concentration with time in an ultrasonic emulsification (Gopal, 1968)

2.1.7.2 Droplet size

The effect of the time factor on the droplet sizes (Scott and Sisson, 1978; Dickinson *et al.*, 1991; Groeneweg *et al.*, 1994) in emulsions has been investigated by several workers (Gopal, 1959) and most investigators agree that prolonging the agitation beyond an optimum time interval does little to improve the quality of emulsions. Under normal conditions of emulsification, the mean droplet size decreases very rapidly in the first few seconds and then gradually attains the limiting value in 1-5 minutes (Gopal, 1968). Thereafter, there is no appreciable reduction in size (Fig. 2.1.7.2)

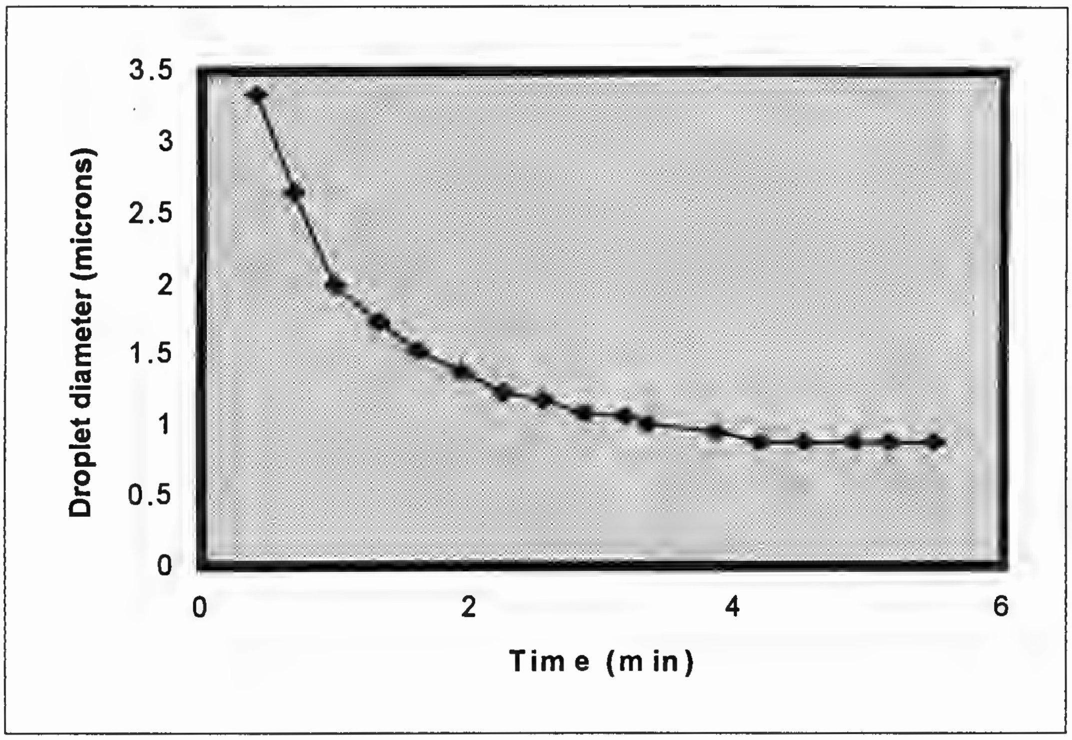


Figure 2.1.7.2: Dependence of droplet size upon time of emulsification (Gopal, 1968)

The stability and viscosity of the emulsions show corresponding variations with the time of agitation.

2.1.7.3 Interfacial area

Emulsion formation in simple mixers has been the subject of many detailed studies (Vermeulen *et al.*, 1955; Rodger *et al.*, 1956; Hüttig and Stadler, 1957; Pavlushenko and Yanishevskii, 1959; Rodriguez *et al.*, 1961; Landau and Prochazka, 1964). It has been found that generally, the interfacial area increases with the increase of the rotational speed and the diameter of the stirrer, and with the decrease of the diameter of the container (Cameron *et al.*, 1991). The interfacial area shows a pronounced increase with the density difference between the dispersed and the continuous phases. The interfacial area also increases with the decrease in interfacial tension (Sumner, 1954; Sherman, 1968).

2.1.7.4 Viscosity

Higher viscosities of the continuous phase, the interface and the bulk emulsion increase emulsion stability (Gladden and Neustadter, 1972; Das *et al.*, 1992). However, the increase in the viscosity of the dispersed phase leads to a decrease in emulsion stability (Nielsen *et al.*, 1958; Smoluchowski, 1971; Wilson, 1994).

2.2 WOOD PRESERVATION

2.2.1 Wood

Wood is one of the most important renewable natural resources (Currie, 1983). About one-third of the land surface is covered by forests (Fengel and Wegener, 1989; Loieau, 1994). Thousand of years ago, wood was used for fuel, tools, and also as a building material. Wood has also been used as a chemical raw material for the production of charcoal, tar/pitch, and potash. As a modern raw material, wood is used for the production of pulp/paper, fibres, films, additives, and many other products (Fengel and Wegener, 1989).

Wood consumption has increased worldwide, accelerated by overfelling and fire clearing. Therefore, for the protection of forests and lowering of wood consumption, the utility of wood must be prolonged by suitable measures. Wood can undergo physical, thermal, and chemical changes, and can be attacked and destroyed by fungi, insects, and marine animals. Wood with a moisture content of less than 18 - 20 % is not attacked by fungi, but can be attacked by insects in certain climates, often predominantly by termites. If constructive wood preservation measures are not possible, or durable and weather-resistant types of wood are not available, chemical preservatives must be used.

2.2.2 Wood treatment

Various wood preservatives and wood treatment processes will be discussed. However, the main focus will be on coal-tar creosote and its wood treatment processes.

2.2.2.1 Wood preservatives

Although preservation can protect wood against weathering and in some instances fire, the main purpose of wood preservation is to protect the wood against biological attacks. Preservation may enhance the service life of wood by 20-50 times (Conradie and Pizzi, 1984) depending on the type of commodity and the end use environment.

Wood preservatives should be chemically stable, should readily penetrate into the wood, and should be resistant to leaching out and evaporation. The environmental pollution during use and processing of preserved wood should be minimal. Wood preservatives can be divided into the following categories:

(A) Coal tar creosote
(B) Water-borne preservatives
(C) Organic solvent preservatives

2.2.2.1.1 **Coal tar creosotes** (see also Chapter 1)

Coal-tar creosote (Watkins, 1967; SABS 538-1980, Brink, 1983) within the distillation range of 200-400 ^{0}C is one of the most important wood preservatives (Pizzi *et al.*, 1984; Mueller *et al.*, 1989; Pommer, 1996, British Standard 144,1997) and has a broad spectrum of activity. For more than 150 years, creosote has been used to protect railway ties, masts, poles, and wood for cooling towers and for marine timber.

Creosote consists mainly of polyaromatic hydrocarbons, viz., acenaphthene, fluorene, phenanthrene, and anthracene (Jamieson 1978). Creosote fractions with a higher boiling range are used for wood preservation in contact with soil or water because of the better long term protection. Middle distillate fractions are suitable for wood subjected to less demanding conditions (British Standard 144,1997). The creosote is usually applied to wood by using the pressure process (Loieau, 1994).

Because of their strong odour, colour, and tendency to sweat (Watkins *et al.*, 1992) on impregnated wood, creosotes can be employed only for outdoor use.

2.2.2.1.2 **Water-borne preservatives**

These preservatives constitute formulations of either organic or inorganic origins. They differ from each other in their activity spectra, their leaching resistance, their impregnation processes and therefore the final use of the treated wood. The most important water-borne wood preservatives are those that are rendered insoluble by the reaction of the components with one another in the wood and those that become tightly bonded to the wood fibers, so that they are resistant to being leached out.

Water-borne preservatives can be divided into the following groups:

- inorganic salt mixtures that are fixed in the wood by chromium(VI) compounds. During fixation in the wood, chromium(VI) compounds are reduced to almost insoluble chromium(III) compounds (Pizzi, 1980, 1982a; Loieau, 1994; Pommer, 1996) and

- organic compounds that are applied to wood in the aqueous phase and become bonded to the fibers or are precipitated to form insoluble compounds in the wood.

Water-borne preservatives are usually applied by the pressure process. However, tank and butt-end treatment processes can also be used. Other water-borne preservatives e.g. certain fluorine and boron compounds are not fixed in the wood and can therefore be used to protect only wood that is not exposed to moisture. Other examples of the water-borne preservatives include arsenic-containing compounds which have broad-based activity even against termites. The arsenic-containing wood preservatives are also resistant to being leached out of the wood. Because of toxicological reasons (Kromhout, 1983) , arsenic compounds are usually substituted by more environmentally friendly chemicals e.g. fluorine, boron, copper (Pizzi, 1982b), ammonium, N-cyclohexyldiazenium chelates, phenol derivatives, etc. Of all the compounds used to substitute arsenic, the alkylammonium compounds offer a considerable potential as wood preservatives.

2.2.2.1.3 Solvent-borne wood preservatives

These preservatives consist of active ingredients, an insecticide and/or a fungicide, dissolved in an organic solvent. The advantage of using these preservatives is that a second coat can be applied to the protected wood, which is not possible for wood treated with heavy oil-containing preparations. Treatment with these preservatives also gives long lasting protection due mainly to their natural insolubility in water. After being carried into the wood by an organic solvent, the latter evaporates, leaving the active ingredient. Depending on the purpose envisaged, solvent-borne preservatives frequently contain mixtures of various active substances, pigments, dyes, light stabilizers, and water repellents. Solvent-borne preservatives penetrate wood without altering its structure (dimensions). The preservatives can be applied by brushing, injecting, spraying, dipping, or the double vacuum process with or without pressure (see 2.2.2.2).

2.2.2.2 Methods of applying wood preservatives (Loieau, 1994)

The successful treatment of any timber preserving process requires that the preservative penetrates evenly into the wood to a sufficient depth. The concentration of the preservative in the wood should also protect the wood from destroyers in the environment in which it is to be used.

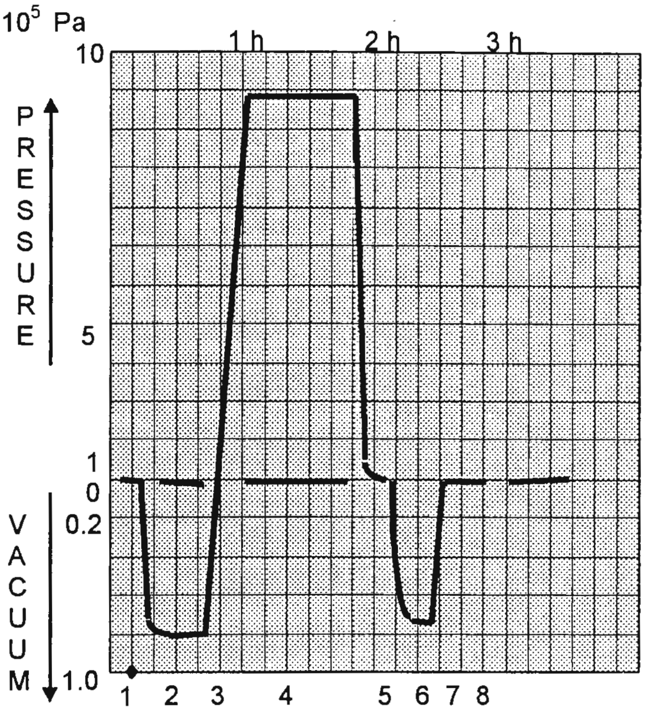
Different treatment methods are applied to seasoned and unseasoned timber. "Seasoning" is the controlled removal of moisture from wet or "green" wood. Seasoned timber has many attributes e.g. it is lighter and therefore cheaper to transport, it is stronger and less liable to insect and fungal attack, etc. More importantly, seasoned timber usually accepts preservatives more readily because there is space in the wood.

2.2.2.2.1 Treatments for seasoned timber

a) Pressure processes

The most effective method of preservative treatment of wood is the use of pressure impregnation. The amount and duration of pressure needed depends on the species and the penetration required. The usual pressure applied is between 800 and 1400 kPa. Several types of high pressure processes are used for wood impregnation. These processes include, the full cell (Bethel), the empty cell, and the oscillating and alternating pressure methods.

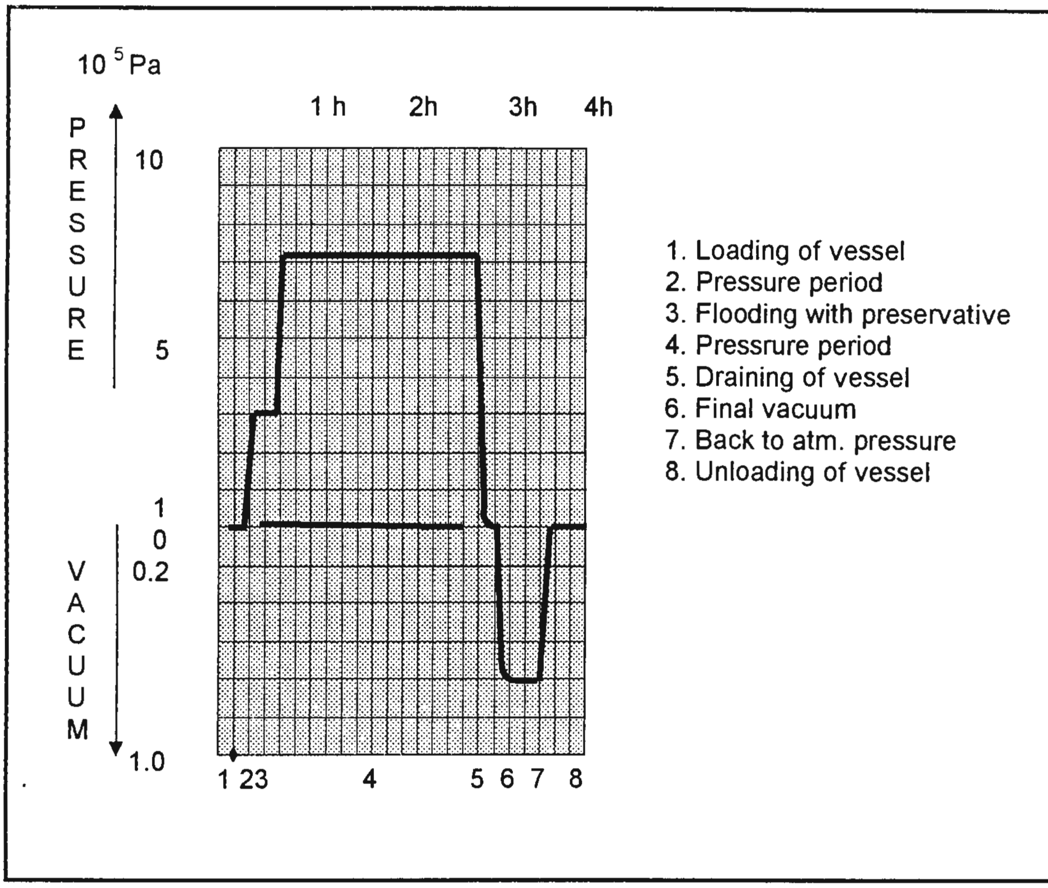
The Full cell or Bethel process - The aim of the full cell treatment is to fill the cells of the wood with the preservative so that the maximum amount can be retained. Water-borne preservatives are often used in this process. Creosote is also used when a high retention is required. Creosote is heated to between 80 to 110 ^{0}C (Loieau, 1994) during the pressure period to lower the viscosity, and improve the penetration. The main steps in the full cell process are illustrated below;



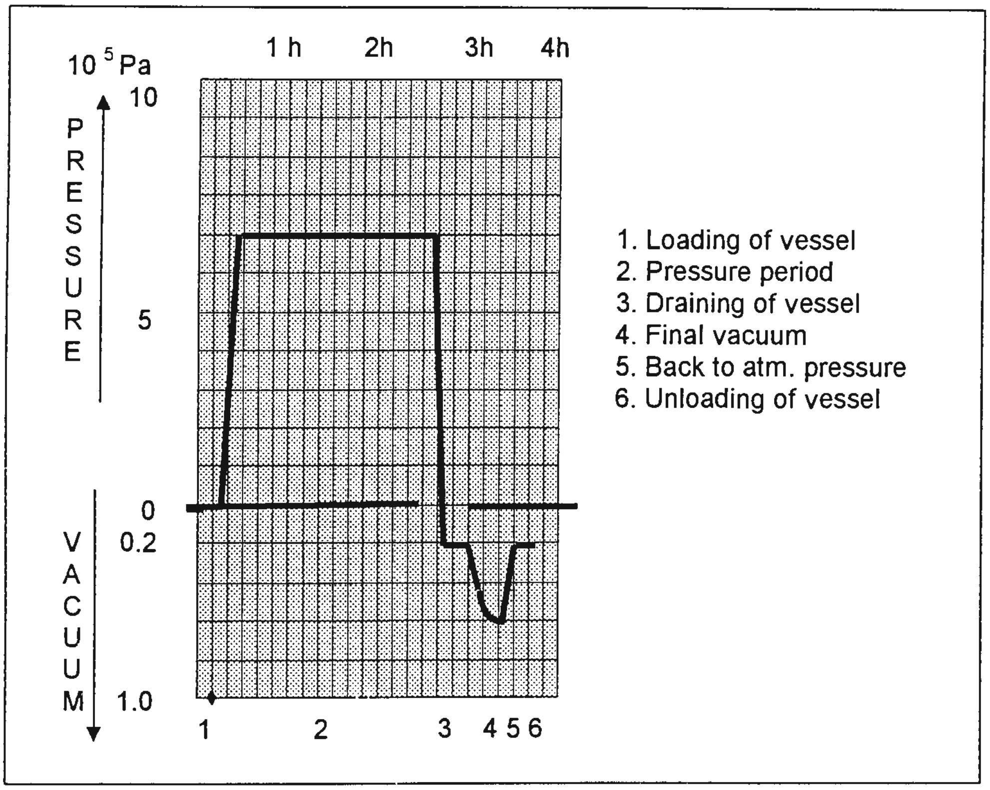
1. Loading of vessel
2. Initial vacuum
3. Flooding with preservative
4. Pressure period pressure
5. Draining of vessel
6. Final vacuum
7. Back to atmospheric
8. Unloading of vessel

Figure 2.2.2.2.1a: Full cell process (Loiseau, 1994)

The Empty cell processes - There are two main types of empty processes, viz., Rüping and Lowry processes named after their inventors. In contrast to the full cell, both processes do not have an initial vacuum applied. Instead, the preservative is forced into the wood under pressure and then a vacuum is applied to remove excess preservative. Empty cell processes are applicable where a deep penetration is required with a limited final retention. This process uses oil based preservatives. The main steps of the two processes are illustrated below;


10 5 Pa
PRESSURE
10
5
1
0
0.2
VACUUM
1.0
1 h 2h 3h 4h
1 23 4 5 6 7 8
1. Loading of vessel
2. Pressure period
3. Flooding with preservative
4. Pressrure period
5. Draining of vessel
6. Final vacuum
7. Back to atm. pressure
8. Unloading of vessel

(i)



(ii)

Figure 2.2.2.2.1b: (i) Rüping treatment, (ii) Lowry treatment (Loiseau, 1994)

Oscillating and Alternating pressure methods - The oscillating pressure method (OPM) is used to treat either freshly felled timber or seasoned wood with water-borne preservatives. It uses repeated cycles of pressure and vacuum. OPM treatment can be preceded by steaming which helps to reduce the wood moisture content and to improve permeability. A variation of OPM is the alternating pressure method (APM). This method uses repeated applications of high pressure and atmospheric pressure with no vacuum.

Double vacuum process - The double vacuum process is similar to the full cell process, but the former uses about one-tenth of the pressure involved in the full cell process.

Other treatment processes for seasoned timber include the solvent processes and processes that dot not require pressure vessels. In the solvent processes, low flash point organic solvents are used to carry the preservative into the wood, leaving the product completely dry. These solvents are ultimately recovered.

b) Processes not requiring pressure vessels

Insertion of solid and paste preservatives into pre-drilled holes or splits in the wood. - Typically these preservatives contain water soluble substances and are activated or released when pre-treated wood becomes wet.

Brushing, spraying, and deluging of liquid preservatives and spreading of paste preservatives. - These processes are used for liquid preservatives based on organic solvents or low viscosity tar oils. The low surface tension of such liquids enable the preservative to creep into seasoned wood and creates an envelop of protection against infestation. The paste preservatives are spread onto the timber surface by hand or are pumped through a lance with a suitable spreading nozzle.

Dipping or immersion - All three types of preservatives (creosote, water-borne, and solvent-borne) can be applied to wood by dipping or immersion. Although resulting in lower preservative absorption and less penetration than the pressure processes, this method provides timber with a good degree of protection against attack by creating a complete envelop of treatment.

Hot and cold method (Thermal process) using creosote - Thermal processing offers a very satisfactory method of impregnation. In this process, seasoned timber is immersed completely or partially in a bath of preservative which is heated for a few hours and allowed to cool while the timber is still submerged in the liquid. During the heating period, the air in the cells of the wood expand and most of it is expelled as bubbles. During the cooling period, the air remaining in the cells contracts creating a vacuum and the preservative is drawn into the wood. The whole absorption takes place during the cooling period. The temperature of the hot bath is normally 80 to 95 ^{0}C.

2.2.2.2.2 Treatment for unseasoned timber

The treatment of unseasoned timber takes place at many stages or transformation of wood. There is provisional treatment for freshly felled logs designed to protect them from biological attacks during different steps of processing from felling to seasoning. The following are examples of treatments protecting unseasoned wood against biological decay and antisapstain.

Dip-diffusion treatment - The principle of this method is that when a highly water soluble preservative is applied in concentrated form to the surface of very wet timber, it tends to dilute itself in water of the wood cells and diffuses gradually inward from the surface.

Pressure/Diffusion processes - Unseasoned wood may be steamed and then quenched by a cool treating preservative. As air in the wood contracts, the temperature drops and draws the preservative solution in. The main limitation of diffusion preservatives is that they are not fixed in the wood by chemical reactions and can therefore be leached out in wet conditions.

Sap displacement methods - This method can only be applied to round timber in green condition. It uses hydrostatic pressure from gravity or applied pressure to force the preservative into the sapwood band at the butt end.

3 EXPERIMENTAL

3.1 INTRODUCTION

The middle distillates (range 200 – 280 °C) of creosote (hereafter called medium creosote) and the surfactants used in all experiments were first characterized. The medium creosote was characterized by determining its HLB. The surfactants were characterized by determining their CMC. The surfactants that are suitable for the emulsification of medium creosote were then identified and these surfactants were used in all other experiments.

3.2 EMULSION

3.2.1 Materials

3.2.1.1 Oil phase

Medium creosote was used in all laboratory experiments. SAK 100, which is a mixture of medium creosote, heavy creosote (270 - 380 ^{0}C), and residue oil (290 - 440 ^{0}C) in specific ratios was used in the pilot scale experiment. SAK 100 was used in order to obtain more representative results because SAK 100 is used as a commercial wood preservative. Table 3.2.1.1 gives the main components of medium creosote.

Table 3.2.1.1

The main components of medium creosote (% m/m))(Haasbroek, 1996)

Phenol and Phenol derivatives	32
Naphthalene and Naphthalene derivatives	31
Paraffins	7
Olefins	6
Benzofurans	7
Fluorenes	4
Heteroatomic compounds	2
Other compounds	11

3.2.1.2 Aqueous phase

Chemically pure NaOH pellets and distilled water were used in the preparations of all aqueous phases.

3.2.1.3 Surfactants

Only anionic and nonionic surfactants were evaluated because of their widespread use, availability, and low costs. Six different chemical types (Table 3.2.1.3) with three types falling under anionic surfactants and the other three falling under nonionic surfactants were evaluated. The detail list of all the surfactants that were evaluated is given in Section B.

Table 3.2.1.3

Chemical types of surfactants evaluated

Class of surfactant	Chemical type of surfactant
Anionic	1) Fatty acid soaps 2) Sulphosuccinates and Sulphosuccinamate 3) Alkyl aryl sulphonates
Nonionic	1) Sorbitan esters 2) Polyoxyethylene sorbitan esters 3) Oxoalcohol ethoxylates

Fatty acid soaps - Soaps of the following compounds were prepared according to the saponification method in Appendix III; castor oil, linseed oil, oleic acid, and stearic acid. Chemically pure linoleic acid (99 %), linolenic acid (99 %), ricinoleic acid (99 %), palmitic acid (90 %), rosin gum, crude tall oil and distilled tall oil (R30-5) were used in the *in situ* saponification method. (Tiwari and Sharma, 1970; Spitz, 1996).

Sulphosuccinates and Sulphosuccinamate, Alkyl aryl sulphonates, Sorbitan esters, and Polyoxyethylene sorbitan esters - The following compounds were evaluated; chemically pure Aerosol A 196, and Aerosol OT-B (sulphosuccinates) and Aerosol 22 (sulphosuccinamate); Nansa YS 94, Nansa SS 30, and HAC (alkyl aryl sulphonates); a range of chemically pure sorbitan esters (Span 20, Span 40, Span 60, Span 65, Span 80, and Span 85) and polyoxyethylene sorbitan esters (Tween 20, Tween 40, Tween 60, Tween 65, Tween 80, and Tween 85).

Oxoalcohol ethoxylates - AM 13 and AM 14 were synthesized by reacting the oxoalcohols with ethylene oxide at 140 ^{0}C using NaOH as a catalyst (Porter, 1994).

3.2.2 Processes

3.2.2.1 Characterization of medium creosote - HLB

The "required HLB" of medium creosote was theoretically estimated using the reference tables (Appendix I) (Smook, 1988).

Sorbitan esters (Span range) and polyoxyethylene sorbitan esters (Tween range) were used for the practical determination of the "required HLB" for the medium creosote. Span and Tween blends with the following HLB values (ICI, 1984) were prepared:

Table 3.2.2.1

Span/Tween blends and their respective HLB values (ICI, 1984)

Span/Tween blend ratios	HLB
Span 85/Tween 85 - (100 : 0)	1.6
Span 65/Tween 65 - (85 : 15)	3.2
Span 65/Tween 65 - (70 : 30)	4.6
Span 65/Tween 65 - (50 : 50)	6.4
Span 65/Tween 65 - (30 : 70)	8.0
Span 65/Tween 65 - (15 : 85)	9.2
Span 65/Tween 65 - (0 : 100)	10.4
Span 20/Tween 20 - (70 : 30)	11.0
Span 20/Tween 20 - (50 : 50)	12.6
Span 20/Tween 20 - (40 : 60)	13.4
Span 20/Tween 20 - (30 : 70)	14.3
Span 20/Tween 20 - (15 : 85)	15.5
Span 20/Tween 20 - (0 : 100)	16.7

The Span/Tween blend (B) was then mixed with the medium creosote (MC) to make 5 % (m/m), 20 % (m/m), and 40 % (m/m) of the B/MC mixture. The B/MC mixture was dispersed into the distilled water (W) according to the following B/MC : W ratios;

5:95, 25:75, 50:50, 75:25, and 95:5.

3.2.2.2 Characterization of surfactants - CMC

The critical micelle concentrations (CMC) of the surfactants (only those soluble in water) were measured using a Krüss K 12 tensiometer fitted with a du Noüy platinum ring.

3.2.3 Selection of suitable surfactants

3.2.3.1 Apparatus

The emulsions were prepared using the IKAMEG RCT magnetic stirrer with a 40 mm bar stirrer. The emulsions were stirred for 5 minutes at room temperature and atmospheric pressure.

3.2.3.2 Selection process

The surfactants that are suitable for the emulsification of medium creosote were screened by preparing a mixture consisting of an excess of the surfactant (20 % (m/m) of the weight of medium creosote). This mixture (M) was then dispersed into the distilled water (W) using the following M : W ratios: 5:95, 25:5, 50:50, 75:25, and 95:5. The surfactants which could successfully disperse medium creosote in water, in a form of milky-white or milky-pink or light-brown emulsions were then identified. Only these surfactants were used further. These surfactants included saponified castor oil, R30-5, and crude tall oil. Because of economic reasons and also because R30-5 is a refined fraction of crude tall oil, only saponified castor oil and crude tall oil were further used in all other experiments.

3.2.3.3 The effect of different fatty acids (constituting castor oil and tall oil) on the emulsification of medium creosote

In order to determine the effect of different fatty acids constituting castor oil and tall oil (Dos, 1952) on the emulsification of medium creosote, the different fatty acids were mixed according to their ratios in castor oil and tall oil.

Castor oil - The free fatty acids (constituting castor oil) in Table 3.2.3.3a were mixed together and saponified according to the saponification procedure in Appendix III.

Table 3.2.3.3.a

Fatty acids constituting castor oil

Fatty acid	Concentration (% m/m)
Ricinoleic acid	87.8
Oleic acid	8.0
Linoleic acid	3.6
Stearic acid	0.3

The saponified combination of free fatty acids was evaluated (according to the procedure in 3.2.3.2) for the emulsification of medium creosote. Saponified castor oil was used as a standard.

Ricinoleic acid was then left out of the mixture formulation of the fatty acids. The mixture was saponified and evaluated for the emulsification of medium creosote as above. Finally, ricinoleic acid was also saponified and evaluated for the emulsification of medium creosote as above.

Tall oil - The free fatty acids and rosin gum (constituting distilled tall oil (R30-5)) in Table 3.2.3.3.b were mixed together and evaluated as a surfactant for the emulsification of medium creosote according to the procedure in 3.2.3.2. R30-5 was used as a standard.

Table 3.2.3.3b

Fatty acids constituting distilled tall oil (R30-5)

Fatty acid	Concentration (% m/m)
Oleic acid	30
Linoleic acid	28
Linolenic acid	4
Stearic acid	2
Palmitic acid	1
Rosin gum	30

The above fatty acids were then evaluated individually as surfactants for the emulsification of medium creosote. The following combinations of fatty acids in equal proportions were also evaluated;

- Oleic acid + Linoleic acid
- Oleic acid + Linoleic acid + Linolenic acid
- Oleic acid + Linoleic acid + Linolenic acid + Rosin gum
- Oleic acid + Linoleic acid + Linolenic acid + Rosin gum + Stearic acid
- Oleic acid + Linoleic acid + Linolenic acid + Rosin gum + Stearic acid + Palmitic acid

3.2.4 Mode of adding the surfactant

The three different modes of adding the surfactant that were used in different emulsion systems are given in Table 3.2.4.

Table 3.2.4

Modes of adding the surfactant used for different emulsion systems

Emulsion system	Mode of adding surfactant
Aqueous continuous phase	Surfactant-in-water
Oil continuous phase	Surfactant-in-oil
Crude tall oil as surfactant	nascent soap

3.2.5 Emulsion preparation

3.2.5.1 Apparatus

The emulsions were prepared by mixing the oil phase with the aqueous phase and vigorously shearing at 7000 r.p.m. using a Silverson L4R multipurpose laboratory emulsifier for 30 minutes. The average droplet size distribution of emulsion formulations was estimated using an Olympus B061, 1000 X magnification microscope fitted with a TV screen and a Malvern analyzer.

3.2.5.2 Identification of a suitable emulsion formulation

Different emulsion formulations were prepared using saponified castor oil (SCO) and crude tall oil (CTO) (Identified in 3.2.1.2c as suitable surfactants for the emulsification of medium creosote). The initial formulations were prepared by mixing the oil phase and the aqueous phase in a 50:50 ratio (m/m) with the surfactant making 20 % of the oil phase. These formulations were optimized by varying the amount of each component of the formulation under investigation.

Table 3.2.5.2a

Phase composition of medium creosote emulsion formulations

Oil phase	Aqueous phase
1) Medium creosote Saponified castor oil	Distilled H_2O
2) Medium creosote Crude tall oil	Distilled H_2O NaOH

Suitable emulsion formulations were identified based on stability and visual examination (quality). The stability of the formulations was measured by determining the rate at which the oil and the aqueous phases separated in a 10 ml measuring cylinder.

The effect of the surfactant concentration on the droplet size distribution of the medium creosote emulsions was investigated by measuring the droplet size distribution of four SCO/medium creosote emulsions with different SCO concentrations. The droplet size distributions of these medium creosote emulsions were measured by a Malvern analyzer. The emulsion formulations in Table 3.2.5.2b were used;

Table 3.2.5.2b

Compositions of the formulations (% m/m) used for the determination of the droplet size distribution

Sample	[H_2O]	[SCO]	[MC]
1	15	15	70
2	12	18	70
3	20	20	60
4	16	24	60

3.2.5.3 The effect of the time of agitation on the droplet size distribution

The emulsion formulation consisting of 87 % (m/m) medium creosote (identified in 3.2.3.2) was prepared at 3000 r.p.m. using different shearing time periods (5,10,15, 20, 30, 45, 60, and 75 minutes) in order to investigate the effect of the shearing time on the droplet size distribution. The average droplet size distribution of the resultant emulsions was estimated using an optical microscope. The effect of the time of agitation on viscosity and stability of the emulsion formulation was only qualitatively determined.

3.2.5.4 The effect of the intensity of agitation on the droplet size distribution

The emulsion formulation consisting of 87 % (m/m) medium creosote (identified in 3.2.3.2) was prepared using different shearing speeds (3000, 5000, 7000, and 8000 r.p.m.) for the shearing time period of 30 minutes in order to investigate the effect of the shearing speed on the droplet size distribution.

3.3 WOOD PRESERVATION

Unemulsified medium creosote and unemulsified SAK 100 were used as standards in the laboratory scale and the pilot scale impregnation tests respectively.

3.3.1 Wood

The wood test blocks were obtained from the *pine tree* and they were prepared by cutting small wood blocks (20 X 20 X 50 mm). 8 wood test blocks were used for each batch of laboratory scale impregnation tests.
The impregnation tests of wood poles using the commercial wood preservative (SAK 100) were carried out in order to obtain a more representative indication of the surface condition of the final creosote treated product. The *Eucalyptus grandis* wood test poles (average length : 1800 mm , average diameter : 60-79 mm) were used for the pilot scale impregnation tests. Batches of 11 and 9 poles were used for the impregnation tests with the standard and the SAK 100 emulsion respectively.

3.3.2 Wood treatment

3.3.2.1 Wood impregnation tests of wood test blocks (laboratory scale)

The surfactants and the emulsion formulations identified in 3.2.3.2 and 3.2.5.2 respectively were used to prepare creosote emulsions of both types (W/O and O/W). The medium creosote concentrations [MC] given in Table 3.3.2.1 were used.

Table 3.3.2.1

Medium creosote concentrations in emulsion formulations used for impregnation of wood test blocks

Surfactant	**Crude tall oil**				**Saponified castor oil**			
Emulsion type	**W/O**		**O/W**		**W/O**		**O/W**	
[MC] % (m/m)	87	79	10	18	80	71	11	20

Both types of emulsions were impregnated into the wood test blocks according to the ASTM 1413-76 method. The performance of these emulsions as wood preservatives was measured by monitoring the following properties;

1) Medium creosote retention in the treated wood test blocks;
2) Surface condition of the treated wood test blocks;
3) Permanence of the emulsions in the treated wood test blocks by:
    (a) Drying the treated test wood blocks in the oven for seven days at 49 ^{0}C;
    (b) Weathering tests (ASTM 1413-76). These tests involve immersing the treated wood blocks in distilled water for 1 hour and drying them in the oven at 49 ^{0}C.

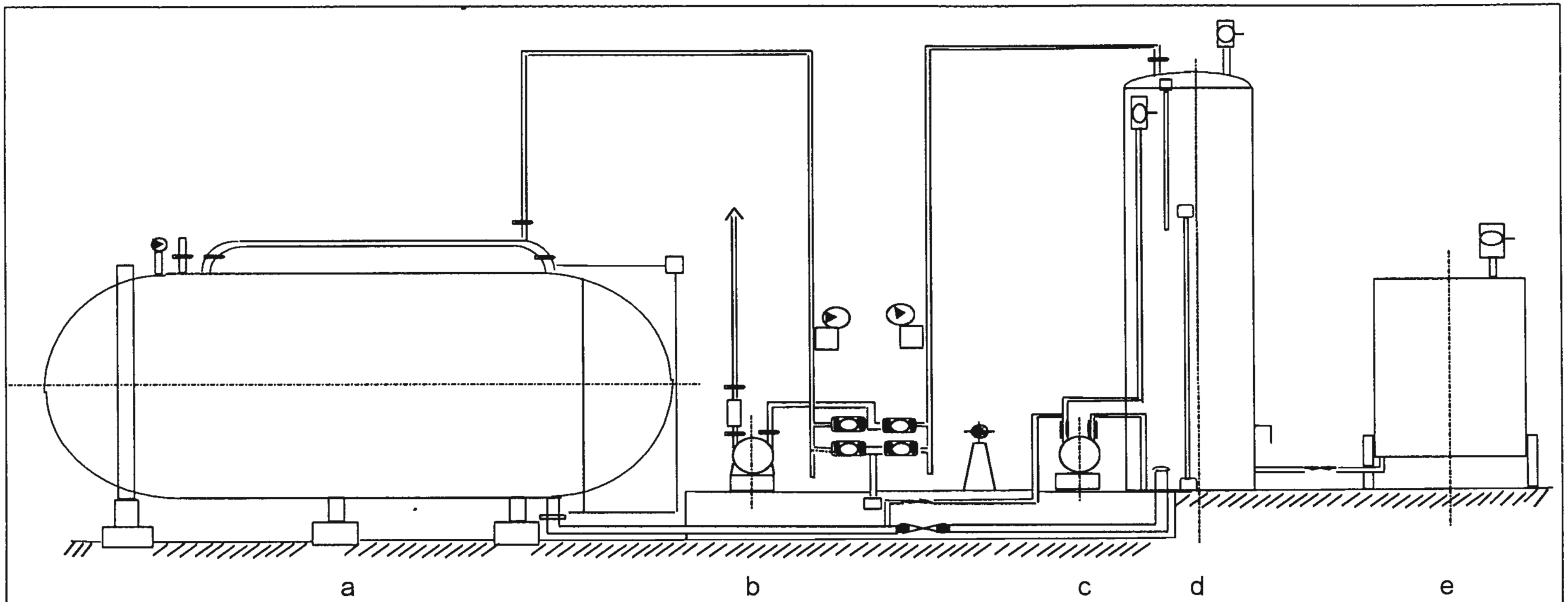
3.3.2.2 Wood impregnation tests of wood test poles (pilot scale)

Only crude tall oil was used as a surfactant for the formulation of the SAK 100 emulsion because of its availability and lower costs compared to the saponified castor oil. The penetration and distribution characteristics of SAK 100/SAK 100 emulsion in the wood poles were determined by sawing through each pole at three different positions, i.e., 150 mm from each end and at the centre of the pole. The average of these three values was then calculated for each pole. The radial penetration of SAK 100/SAK 100 emulsion was then measured by a ruler.

3.3.2.2.1 Apparatus

The pilot plant for the full-cell (Bethel) impregnation process (see Appendix II for operating procedures) was used for the impregnation tests of the wood test poles. The dimensions of the impregnating vessel of the pilot plant were as follows;

length : 2000 mm and radius : 300 mm .



a) Impregnating vessel b) Vacuum pump c) Pressure pump d) Storage and measuring vessel e) Mixing vessel

Figure 3.3.2.2.1 : Schematic diagram of a pilot plant for the full-cell process (Pommer, 1996)

3.3.2.2.2 Preparation of emulsion

The aqueous phase was prepared by dissolving 0.5 % (m/m) NaOH in 10.5 % (m/m) H_2O. The oil phase was prepared by mixing 87 % (m/m) SAK 100 with 2 % (m/m) crude tall oil in a mixing tank of the pilot plant. The aqueous phase was then introduced into the stirred oil phase to make the final emulsion formulation (total mass : 800 kg).

This emulsion formulation was then impregnated into the wood test poles in the impregnation vessel according to the operating procedures of the full cell process (Appendix II).

4 RESULTS AND DISCUSSIONS

4.1 EMULSION

4.1.1 Selection of a surfactant

4.1.1.1 Characterization of medium creosote - HLB

The "required HLB" of medium creosote was theoretically estimated using the ICI's reference tables (Appendix I) to be approximately 14 $\pm$ 1. The higher value of the "required HLB" of medium creosote is due to the high content of aromatics and their derivatives which are assigned higher HLB values (ICI, 1984). This value was further confirmed by the practical determination of the "required HLB " of medium creosote using Span/Tween blends of different HLB values (Table 4.1.1.1).

No emulsions were obtained when the Span/Tween blend (B) with the "required HLB "values less than 9.2 were used. For all Span/Tween blends, no emulsions were obtained when the concentrations of the B in B/MC (Span/Tween blend and medium creosote mixture) was 5 %. The "required HLB" values which yielded positive results are given in Table 4.1.1.1.

Table 4.1.1.1

Results of the practical determination of the "required HLB" value medium creosote

Span/Tween blend (B) ratios	HLB	[B] (%) (m/m)	EMULSION	OBSERVATIONS
Span65/Tween65 (15:85)	9.2	20 40	No Yes	Phases remain immiscible Good, stable emulsion (30)*
Span65/Tween65 (0:100)	10.4	20 40	Yes Yes	Unstable (stability < 5 min) Good, stable emulsion (30)*
Span20/Tween20 (70:30)	11.0	20 40	Yes Yes	Unstable (stability < 5 min) Good, stable emulsion (30)*
Span20/Tween20 (50:50)	12.6	20 40	Yes Yes	Unstable (stability < 5 min) Good, stable emulsion (50)*
Span20/Tween20 (40:60)	13.4	20 40	Yes Yes	Unstable (stability < 5 min) Good, stable emulsion (50)*
Span20/Tween20 (30:70)	14.3	20 40	Yes Yes	Unstable (stability < 5 min) Good, stable emulsion (50)*
Span20/Tween20 (15:85)	15.5	20 40	Yes Yes	Unstable (stability < 5 min) Good, stable emulsion (50)*
Span20/Tween20 (0 :100)	16.7	20 40	Yes Yes	Unstable (stability < 5 min) Good, stable emulsion (50)*

* = Stability time (min.) for emulsion

Even though the quality of all medium creosote emulsions prepared using the Span/Tween blends was generally poor, better emulsions were obtained when the Span/Tween blend with the "required HLB" of 13.4 were used. This value gives an indication of the "required HLB" range of medium creosote.

4.1.1.2 Characterization of surfactants - CMC

The critical micelle concentrations (CMC) of aqueous surfactant solutions were measured to determine their surface activity properties. Anionics showed lower CMCs than nonionics. The nonionic surfactants that were evaluated (Tween range) are more hydrophilic and thus more soluble in water. This solubility increases the CMC of these surfactants because their surface activity is small (Mittal, 1977a; Porter, 1994). Surfactants with more than one hydrophilic group i.e., Tween 65 and Tween 85 showed the highest CMC values. The CMC values of all the surfactants evaluated are given in Table 4.1.1.2a.

Table 4.1.1.2a

CMC values of anionic and nonionic surfactants evaluated

Surfactant	CMC (mg/l)
Tween 20	8.803 (13.17)*
Tween 60	6.769 (27.09)*
Tween 65	11.574
Tween 85	11.256
Castor oil (NaOH)	8.843
Crude tall oil (NaOH)	5.641
R30-5 (NaOH)	3.598
Linseed oil (KOH)	5.028
Oleic acid (KOH)	5.165 (641.1)*
Stearic acid (KOH)	4.624 (582.0)*

* Literature values (Linfield, 1976a and 1976b; Porter 1994; SIR, 1994)

The literature CMC values of Tween 20 and Tween 60 are comparable to the experimental CMC values (Table 4.1.1.2a). The differences can be attributed to the experimental errors. The literature and experimental surface tensions for Tween 20 and Tween 60 at the CMCs were also comparable (Table 4.1.1.2b). The literature CMC values of the saponified surfactants were different from the experimental values (Table 4.1.1.2a).

Table 4.1.1.2b

Surface tension values (γ) (mN/m) at the CMCs (Linfield, 1976a and 1976b; Porter, 1994; SIR, 1994)

Surfactant	Literature γ	Experimental γ
Tween 20	40	38
Tween 60	43	40

The difference between literature CMC values and experimental CMC values for potassium salts of stearic and oleic acids can be attributed to the low purity of these products (Table 4.1.1.2a). These products were not further purified after saponification whereas the literature values are based on pure compounds. Porter (1994) also found a similar discrepancy between literature CMC values and CMC values of commercial products.

The discrepancy between the literature and experimental CMCs and surface tension illustrates the need to measure these values in a commercial environment rather than to rely on literature values.

4.1.1.3 Screening of surfactants

Fatty acid soaps and alkyl aryl sulphonates from the anionics and sorbitan ester from nonionics were the only chemical types that could successfully emulsify medium creosote. No emulsions were obtained when sulphosuccinates/sulphosuccinamate from anionics, polyoxyethylene sorbitan esters and oxoalcohol ethoxylates from nonionics were used as surfactants.

Fatty acid soaps - Generally, saponified castor oil, crude tall oil, and R30-5 yielded emulsions of good quality and stability. Linseed oil yielded a reddish-brown suspension. No emulsions were obtained when oleic acid and stearic acid were used as surfactants. Saponified castor oil yielded emulsions of better quality and stability than both crude tall oil and R30-5. These results further confirm that the "required HLB" of medium creosote falls within the range of 14 $\pm$ 1 because the HLB value of castor oil is also in the range of 14 $\pm$ 1(Appendix I). R30-5 yielded better emulsions than crude tall oil.

Alkyl aryl sulphonates - Nansa SS 30 yielded emulsions of poor quality and stability. HAC yielded a brown suspension. No emulsions were obtained when Nansa YS 94 was used as a surfactant.

The most suitable medium creosote emulsions were obtained by using saponified castor oil as a surfactant. R30-5 yielded emulsions of better quality and stability than crude tall oil. Only Span 20 from the nonionics could successfully emulsify medium creosote even though it yielded emulsions of poor quality and stability.

4.1.1.3.1 The effect of different fatty acids (constituting castor oil and tall oil) on the emulsification of medium creosote

Castor oil - The saponified combination of fatty acids (constituting castor oil) yielded medium creosote emulsions of excellent quality and stability. The emulsions were milky white. These emulsions were more or less similar to those produced by the saponified castor oil. These results confirmed that the combination of fatty acids prepared was close to that of castor oil.

There were no emulsions obtained when the combination of fatty acids without ricinoleic acid was used as a surfactant for the emulsification of medium creosote. However, saponified ricinoleic acid alone yielded medium creosote emulsions of excellent quality and stability. These emulsions were also more or less similar to those produced by castor oil. This implies that ricinoleic acid is the most effective fatty acid in ***castor oil*** for the emulsification of medium creosote.

Distilled tall oil (R30-5) - The combination of free fatty acids and rosin gum (constituting R30-5) yielded medium creosote emulsions of good quality and stability. These emulsions were also similar to those produced by R30-5. This implies that the combination of fatty acids and rosin gum was close to R30-5.

Medium creosote emulsions of various quality and stability were obtained when the following free fatty acids were used as surfactants;
oleic acid, linoleic acid, linolenic acid, and rosin gum. It should be noted that whilst the saponified oleic acid could not emulsify medium creosote (see 4.1.1.3), the nascent soap (*in situ* saponification) method with oleic acid could emulsify medium creosote. Generally, linoleic acid and linolenic acid yielded emulsions of better quality than oleic acid and rosin gum.

There were no emulsions obtained when stearic acid and palmitic acid were used as surfactants for the emulsification of medium creosote. These fatty acids yielded a solid mixture with medium creosote that was very difficult to disperse in water.

Different combinations of free fatty acids and rosin gum (constituting R30-5) produced medium creosote of various qualities. The quality of the medium creosote emulsions when stearic acid and palmitic acid were used in combination with other fatty acids was inferior to the quality of the emulsions produced when the combinations of fatty acids without stearic acid and palmitic acid were used. For a more efficient surfactant for the emulsification of medium creosote, the concentration of stearic acid and palmitic acid, should be kept as low as possible.

Generally, the order of efficiency (in terms of the quality and the stability of the resultant emulsions) of the fatty acid soaps evaluated for the emulsification of medium creosote is as follows;

Saponified castor oil (0.3%)* > R30-5 (3%)* > Crude tall oil (3%)* > Linseed oil (8%)*

* concentration (% m/m) of stearic acid and/or palmitic acid

Saponified castor oil has the lowest concentration of stearic and/or palmitic acid and it is the most efficient fatty acid soap evaluated for the emulsification of medium creosote. Linseed oil has the highest concentration of stearic and/or palmitic acid and it is the least efficient fatty acid soap. This means that the efficiency of the fatty acid soaps as surfactants for medium creosote decreases with the increase in the concentration of stearic and/or palmitic acid.

Palmitic acid and stearic acid are the only saturated fatty acids amongst all the fatty acids evaluated. All other fatty acids contain one or more double bonds in their hydrophobic portion. Therefore, a fatty acid with at least one double bond in its hydrophobic portion is required for the successful emulsification of medium creosote. This observation can be explained by the high degree of unsaturation or aromaticity in medium creosote (Haasbroek, 1996). The unsaturated hydrophobic portion of the fatty acid is therefore more suitable for the emulsification of medium creosote than the corresponding saturated hydrophobic portion.

The low stability shown by the medium creosote emulsions in general, can also be explained by their high degree of unsaturation or aromaticity. (Davis and Smith, 1976).

4.1.2 Identification of a suitable emulsion formulation

The formulations (% m/m) in Table 4.1.2a produced suitable medium creosote emulsions in terms of stability and quality of the emulsions.

Table 4.1.2a

Emulsion formulations suitable for the emulsification of medium creosote

Surfactant	Crude tall oil (CTO)				Saponified castor oil (SCO)			
Emulsion type	W/O		O/W		W/O		O/W	
Formulation	1	2	3	4	5	6	7	8
Medium creosote	87	79	10	18	80	71	11	20
CTO	2	2	2	2	-	-	-	-
SCO	-	-	-	-	9	9	9	9
H_2O	10	18	87	79	11	20	80	71
50% NaOH	1	1	1	1	-	-	-	-
Stability (min)*	20	18	31	23	102	56	>360	>360
Average droplet size (μ)	3	4	5	7	3	5	5	3

* Stability determined at room temperature

Table 4.1.2b

Average droplet size distribution (ADSD) of SCO, W/O medium creosote emulsions (Malvern analyzer)

Sample	**[H_2O] (%m/m)**	**[SCO] (%m/m)**	**[MC] (%m/m)**	**ADSD (μ)**
1	15	15	70	70.0
2	12	18	70	0.5
3	20	20	60	0.4
4	16	24	60	0.4

Generally, the stability and quality of the medium creosote emulsions increases with an increase in the amount of surfactant in the formulation and with a decrease in droplet size distribution. When the SCO concentration in W/O medium creosote emulsions was increased from 9 % to 24 % (m/m), the droplet size distribution of these emulsions decreased from 5.0 to approximately 0.4 μ (Tables 4.1.2a and 4.1.2b). The stability of the emulsion increases with the decrease in droplet size distribution (Sumner, 1954; Kumar *et al.*, 1996; Yan and Masliyah, 1997).

However, an optimum amount of the surfactant should be added in order to avoid creaming of the emulsion and re-emulsification after wood treatment. The stability of the W/O emulsion decreases with the increase in water concentration and the stability of the O/W emulsion decreases with the increase in medium creosote concentration.

Even though the concentration of NaOH does not significantly affect the stability of both types of emulsions, the stability increases slightly with the concentration of NaOH. A minimum concentration of 20 % NaOH solution is required for the successful saponification of the fatty acids in the surfactants.

The O/W emulsions showed better stability than the W/O emulsions for both surfactants (CTO and SCO). This trend was more predominant in SCO emulsion systems. This can be explained by the fact that the CMC of SCO is higher than the CMC of CTO and therefore the solubility of SCO in water should be higher than that of CTO.

4.1.3 The effect of the time of agitation on the droplet size distribution

The results of the effect of shearing time on the droplet size distribution are given below;

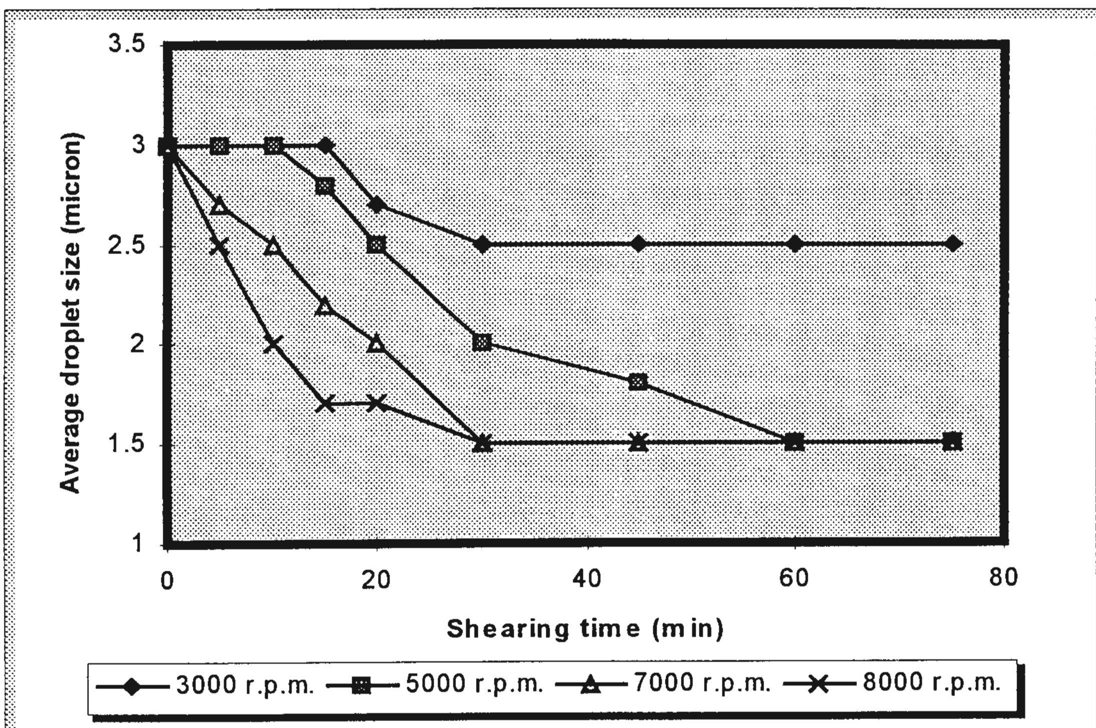


Figure 4.1.3 : The effect of the time of shearing on the droplet size distribution of the medium creosote emulsion

For the shearing speeds lower than 5000 r.p.m., A significant reduction in the droplet size distribution of medium creosote emulsions starts after 15 minutes of shearing. At higher shearing speeds i.e., above 7000 r.p.m., the reduction in droplet size distribution occurs within a few seconds of shearing. For all shearing speeds, no significant reduction in droplet size distribution occurs after 30 minutes. The droplet size distribution of medium creosote emulsions reaches a limiting value after 30 minutes.

4.1.4 The effect of the intensity of agitation on the droplet size distribution

The results of the effect of the intensity of agitation on the droplet size distribution are given below;

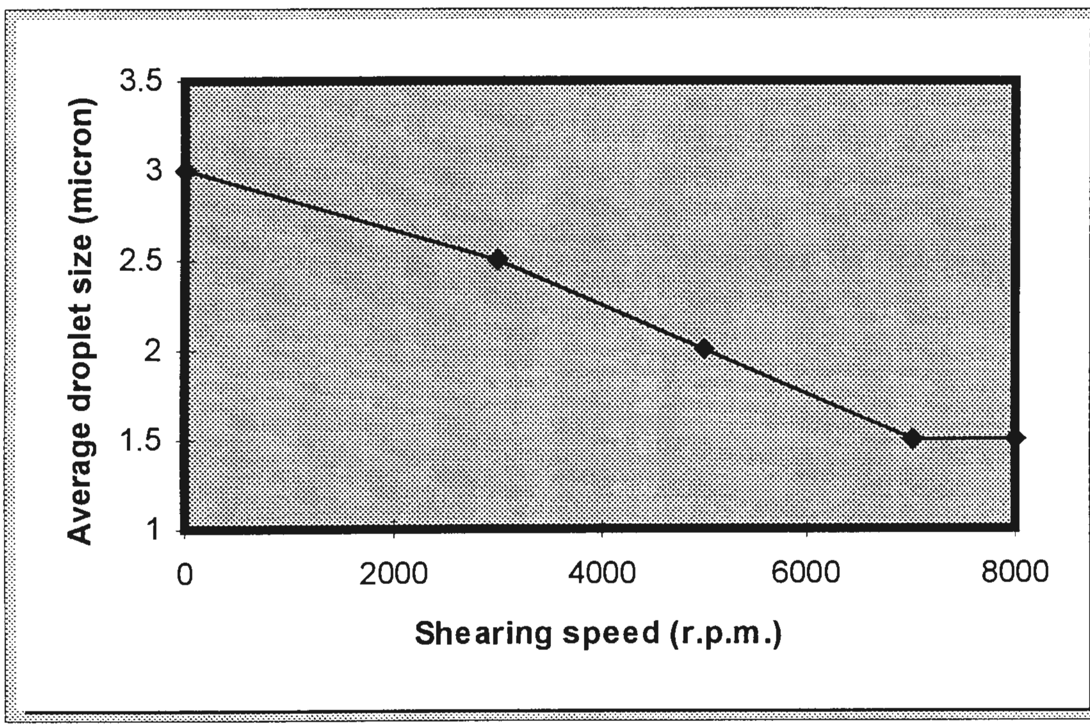


Figure 4.1.4 : The effect of the intensity of agitation on the droplet size distribution of medium creosote emulsion

The droplet size distribution of the medium creosote emulsions decreases with the increase in the intensity of shearing. Finer droplets can be obtained by shearing at higher speeds.

Generally the viscosity and stability of the medium creosote emulsions increases with the decrease in droplet size distribution.

4.2 WOOD PRESERVATION

4.2.1 Wood treatment

4.2.1.1 Impregnation tests of wood blocks with medium creosote emulsions (laboratory scale)

Table 4.2.1.1 gives the results obtained by impregnating wood test blocks with O/W and W/O medium creosote emulsions.

Table 4.2.1.1

Results obtained from impregnation of wood test blocks

Surfactant	CTO				SCO				MC
Type of emulsion	W/O		O/W		W/O		O/W		-
[Medium creosote] (m/m%)	87	79	10	18	80	71	11	20	100
Emulsion retention (kg/m^3)	73	64	93	99	61	71	75	74	-
MC retention (kg/m^3)	64	50	9	18	49	57	8	15	58
%Weight of MC lost after drying for 7dys	24	25	14	13	20	23	19	17	24
MC retention after weathering (kg/m^3)	49	38	8	15	36	38	6	12	44
Swelling & cracking*	NO	NO	YES	YES	NO	NO	YES	YES	NO

* By visual inspection

During impregnation, O/W emulsions produced better emulsion retention than W/O emulsions. However, for the W/O emulsions the medium creosote retention calculated from the emulsion formulations were far better than those of O/W emulsions. The medium creosote retention for O/W emulsions (8-18 kg/m^3) seem to be too low for effective wood preservation.

All treated wood blocks showed "clean" surfaces. There were no indications of "creosote bleeding" on these test blocks. Because no defect in surface appearance could be detected on the test blocks, the surface condition of the final treated product was evaluated by the treatment of wood poles with medium creosote emulsions instead of wood blocks.

O/W emulsions showed better permanence than W/O emulsions. This better permanence can be explained by the slower rate of diffusion of water in wood compared to that of petroleum hydrocarbons. It has been proposed (Goldstein, 1977) that the hydrogen bonding ability of the liquid is the major factor that influences its ability of diffusion in wood.

The wood test blocks treated with O/W showed severe swelling and cracking after weathering tests. This is most probably due to a higher concentration of water in these emulsions. W/O emulsions are therefore more suitable for wood preservation than O/W emulsions. For this reason, pilot scale tests were carried out using W/O emulsions.

4.2.1.2 Impregnation tests of wood poles with SAK 100 emulsions (pilot scale)

Even though the wood poles treated with SAK 100 emulsion showed a darker surface than the poles treated with unemulsified SAK 100 (light brownish surface), the poles treated with the emulsion were more tenacious and oily than the poles treated with unemulsified SAK 100. This means that in this work, it was not possible to improve the surface condition of the creosote treated wood using creosote emulsions.

Comparing the pilot scale results to the laboratory scale results confirms that the surface appearance of the wood test blocks does not give a representative indication of the surface condition of the final treated product. Therefore the surface condition of the final product should always be confirmed on a pilot scale.

The retention results obtained from the impregnation tests of the wood poles with SAK 100 emulsion and the unemulsified SAK 100 are given in Table 4.2.1.2.

Table 4.2.1.2

Results of SAK 100 retention obtained from impregnation tests with SAK 100 emulsion and SAK 100

Wood poles	SAK 100 emulsion	SAK 100
Average volume (m^3)	0.0401	0.0399
Mass before treatment (kg)	38.62	33.90
Mass after treatment (kg)	53.24	46.90
Retention (kg)	14.62	13.00
SAK 100 retention (kg/m^3)	365 $\Rightarrow$ 318 *	326
Average penetration (mm)	160	130

* Emulsion formulation consists of 87 % SAK 100

The SAK 100 and SAK 100 emulsions exhibited similar penetration and distribution characteristics. In both cases, the sapwood was completely penetrated but there was no penetration into the hardwood. SAK 100 emulsion showed penetration characteristics of similar magnitude with unemulsified SAK 100.

5 CONCLUSIONS

The main objective of this project was to investigate the possibility of improving the surface condition of the creosote treated wood (i.e., produce "clean" creosote treated poles) by using creosote emulsions. The two critical steps were the development of medium creosote emulsions. These emulsions were successfully developed but they could not improve the surface condition of the final treated wood (i.e., no "clean" poles could be obtained by using these emulsions).

The medium creosote emulsion was successfully developed by identifying suitable surfactants, emulsion formulations and type of emulsion. The following conclusions can be made;

- For the successful emulsification of medium creosote, the anionic class of surfactants is more efficient than the nonionic class. The anionics yield medium creosote emulsions of better quality and stability than the nonionics. This is easily explained by the acidic nature of medium creosote (Haasbroek, 1996; Schuin , 1998), and therefore a better association with a negatively charged surfactant molecule.

- This anionic surfactant must contain an unsaturated hydrocarbon chain. This observation can be explained by a high degree of unsaturation or aromaticity in medium creosote (Haasbroek, 1996), and therefore an unsaturated hydrophobic portion is more compatible with the unsaturated oil phase than with the saturated oil phase (ICI, 1984).

- Amongst different chemical types of anionics evaluated, i.e., fatty acid soaps, sulphosuccinates, sulphosuccinamate and alkyl aryl sulphonates, fatty acid soaps are the most efficient chemical type for the emulsification of medium creosote. Most fatty acid soaps evaluated could successfully emulsify medium creosote. This is partly because none of the anionic surfactants evaluated, other than the fatty acids, have an unsaturated hydrophobic portion. The other reason might be the relatively large sizes of the hydrophilic portions of these other anionics. The smaller size of the hydrophilic portion of the fatty acids should allow for more intimate arrangement of the fatty acid at the phase interface.

- The following fatty acid soaps in order of their emulsifying efficiencies can emulsify medium creosote; castor oil > distilled tall oil (R30-5) > crude tall oil > linseed oil. The following free fatty acids which are contained in all of the above soaps can individually emulsify medium creosote; ricinoleic acid, linoleic acid, linolenic acid, oleic acid, and rosin gum. Stearic acid and palmitic acid are also present in small concentrations in the above soaps. Stearic acid and palmitic acid could not individually emulsify medium creosote and their addition to the combination of other fatty acids has a negative effect on the efficiency of the combination of fatty acids as a surfactant for medium creosote. Furthermore, the most efficient fatty acid soap (castor oil), has the lowest concentration of stearic and/or palmitic acid; and the least efficient fatty acid soap (linseed oil) has the highest concentration of stearic and/or palmitic acid. Therefore, the efficiency of the fatty acid soaps for the emulsification of medium creosote decreases with the increase in concentration of stearic acid and/or palmitic acid.

- The O/W emulsions prepared by using saponified castor oil and crude tall oil were more stable than the W/O emulsions. In both cases, the O/W emulsions were of better quality than the W/O emulsions. However, when the O/W emulsions were used for the wood blocks impregnation tests, they caused severe splitting of wood blocks. Therefore the O/W emulsion formulations are not suitable for wood preservation.

- The pilot scale impregnation tests were carried out using the W/O crude tall oil formulations. The pilot scale impregnation tests showed that the surface condition of the creosote treated wood could not be improved by using creosote emulsions. In fact, the wood treated with creosote emulsions showed a more oily, sticky surface than the wood treated with unemulsified creosote. Penetration and distribution characteristics of both SAK 100 and SAK 100 emulsions were satisfactory. In both cases, the sapwood was completely penetrated but there was no penetration into the hardwood.

- Watkins and co-workers (1992) have patented the development of pigment emulsified high temperature creosote emulsions. They claim that this pigment emulsified creosote (PEC) produces wood poles with "clean" surfaces. Future research work can be directed towards investigating the possibility of using pigments to emulsify medium temperature creosote.

- The possibility of developing and using creosote microemulsions for wood preservation purposes can also be investigated. "Clean" wood surfaces might be achieved by enhanced penetration and distribution characteristics expected from creosote microemulsions. This option might be more challenging considering the problem that might be encountered with the fixation of the microemulsions once they are in the wood.

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APPENDIX I Required HLB values (ICI, 1984)

Table Ia

Required HLB for O/W emulsions of a variety of emulsion ingredients

(Approx. ± 1)

Emulsion ingredient	HLB	Emulsion ingredient	HLB
Acetophenone	14	Diisooctyl Phthalate	13
Acid, Dimer	14	Diisopropyl Benzene	15
Acid, Isostearic	15-16	Dimethyl Silicone	9
Acid, Lauric	16	Ethyl Aniline	13
Acid, Linoleic	16	Ethyl Benzoate	13
Acid, Oleic	17	Fenchone	12
Acid, Ricinoleic	16	Isopropyl Myristate	12
Alcohol, Cetyl	16	Kerosene	12
Alcohol, Decyl	15	Lanolin, Anhydrous	12
Alcohol, Hexadecyl	11-12	Lauryl Amine	12
Alcohol, Isodecyl	14	Menhaden Oil	12
Alcohol, Lauryl	14	Methyl Phenyl Silicone	7
Alcohol, Oleyl	13-14	Methyl Silicone	11
Alcohol, Stearyl	15-16	Mineral Oil, Aromatic	12
Alcohol, Tridecyl	14	Mineral Oil, Paraffinic	10
Arlamol E	7	Mineral Spirits	14
Beeswax	9	Mink Oil	9
Benzene	15	Nitrobenzene	13
Benzonitrile	14	Nonyl Phenol	14
Bromobenzene	13	Orthodichlorobenzene	13
Butyl Stearate	11	Paraffin Wax	10

Emulsion ingredient	HLB	Emulsion ingredient	HLB
Carbon Tetrachloride	16	Petrolatum	7-8
Carnuaba Wax	15	Petroleum Naphtha	14
Castor Oil	14	Pine Oil	16
Chlorinated Paraffin	12-14	Polyethylene Wax	15
Chlorobenzene	13	Propene, Tetramer	14
Corn Oil	8	Styrene	15
Cottonseed Oil	6	Toluene	15
Cyclohexane	15	Trichlorotrifluoroethane	14
Decahydro naphthalene	15	Tricresyl Phosphate	17
Decyl Acetate	11	Xylene	14
Diethyl Aniline	14		

Table Ib

Required HLB for W/O emulsions of a variety of emulsion ingredients

(Approx. ± 1)

Emulsion ingredient	HLB
Gasoline	7
Kerosene	6
Minreal Oil	6

APPENDIX II Wood impregnation procedure (Full-cell process) (de Wet, 1991)

1) Weigh the wood and load it into the impregnating vessel.
2) Draw vacuum for 15 mins. at absolute pressure of 10kPa from the impregnating vessel.
3) Fill the mixing vessel with creosote and set the thermostats in the mixing vessel, measuring vessel, and the impregnating vessel to ± 100 ^{0}C.
4) When the desired temperature (± 100 ^{0}C) in the three vessels has been reached, transfer creosote from the mixing vessel into the measuring vessel; note the level reached by the creosote in the measuring tank.
5) Transfer creosote from the mixing vessel into the impregnating vessel.
6) Using the pressure pump, apply pressure to the impregnating vessel until the desired pressure is reached.
7) Transfer creosote from the impregnating vessel back into the measuring vessel; take note of the level reached by creosote in the measuring vessel.
8) Deppresurise the impregnating vessel by drawing vacuum at 10kPa for 15 mins. from the impregnating vessel.
9) Allow the contents of the impregnating vessel to cool and remove the wood.
10) Weigh the treated wood.

Calculating creosote retention (kg/m^3)

(a) The difference in the creosote level (in the measuring vessel) before and after treatment
(b) The difference in the weight of the wood before and after treament.

APPENDIX III Saponification method (EISCO, 1996)

1) Dissolve 3.85 % (m/m) NaOH in 62.81 % (m/m) of distilled H_2O.
2) Add 33.34 % (m/m) of castor oil/ linseed oil/ oleic acid to make the final mixture.
3) Stir and heat this mixture under reflux until it turns clear.
4) Allow to cool.