

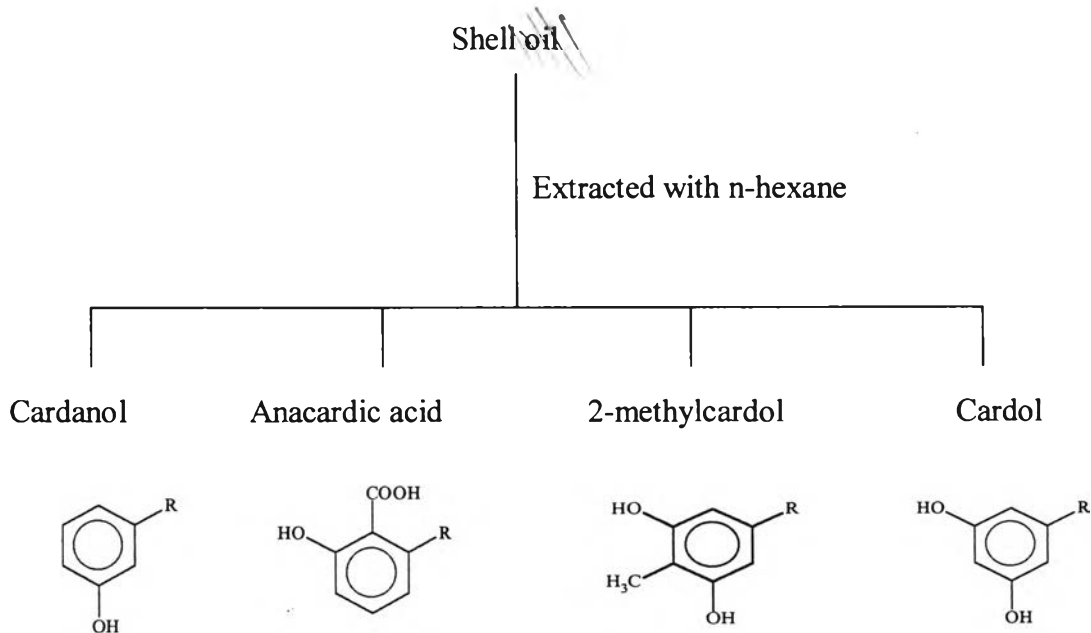
## CHAPTER II

### THEORETICAL

#### 2.1 The Cashew Nut Shell Liquid

Cashew Nut Shell Liquid (CNSL) [1,2] is an oil obtained from the spongy layer between the inner and outer shell of the cashew nuts. The raw liquid comprises mainly anacardic acid (2-carboxy-3-pentadecadienyl phenyl) and related acid of different degree of unsaturation, together with cardol (m-pentadecadienyl resorcinol), 2-methylcardol(5-pentadecylresorcinol) and cardanol (3-pentadecylphenol).

The component of CNSL contains a phenolic hydroxyl group and an unsaturated side-chain : monoene, diene and triene, which is extracted from the shell with hexane as shown below



The CNSL has been used in various industries. Historically the main outlet for CNSL has been in the manufacture of brake linings and surface coating. Other applications include cement and adhesives, laminated board manufacture, insulating vanishes, and impregnating materials, modifier for phenol-based resin, plasticizers, germicides and insecticides, indelible inks, lubricants and preservatives.

## 2.2 Color markers

A dye is defined as a material lending visible color when dissolved in the product such as dyes which have been used for dyeing organic liquid

A marker is defined as a substance which can be dissolved in a liquid to be identified, then subsequently detected by performing a simple chemical or physical test on the tagged liquid. [4]

Both of dye and marker are needed to clearly distinguish chemical or physical similar liquids and they are used to provide visually distinctive brand and grade denominations for commercial and safety reasons such as some lightly taxed product are marked to distinguish them from similar materials subjective to higher taxes. As another example, fuels are marked to deter fraudulent adulteration of premium grade product with lower grade product such as blending kerosene into premium grade gasoline or blending regular grade gasoline into premium grade gasoline, furthermore, blending untaxed diesel into taxed diesel which the purpose of cost reduction.

*Handwritten note:*  
 10/11/11

Dyes alone are not always adequate to securely and reliably identify liquids. Many dyes are easily removed by unauthorized persons and can be obscured by other natural or added substances.

The important characteristics of markers for petroleum fuel are

1. Are entirely foreign to the liquids.
2. Can be supplied as highly concentrated solution in petroleum-compatible solvents.
3. Are easily detected by a simple field test.
4. Are not obscured by unstable natural component of the liquid.
5. Are stable over the anticipated storage life of the tagged liquid.
6. Have identities which can be confirmed by laboratory methods.

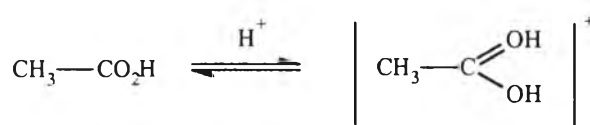
**2.3 Color of substances**

Generally, unsaturated functional group of organic compounds are capable to absorb energy in the form of light. Those functional groups are defined as chromophore, which classified to three groups, non-lone pair electron (e.g.  $\text{O}=\text{C}$ ), lone pair of electron (e.g.  $\text{C}=\text{C}$ ,  $-\text{N}=\text{N}-$ ) and aromatic group [5,6,7]. The chromophore has a function to transfer electron from lower energy level to higher level ( e.g.  $\pi-\pi^*$  ) Thus involve the occurrence. The colority of compounds has more variable upon electron shift, solvent polarity, steric effect and substituents. Some substituents do not absorb light. They are called auxochrome, but effect the absorption spectrum of chromophore. For example,  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ,  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $-\text{OH}$ ,  $-\text{OR}$  and halogen.

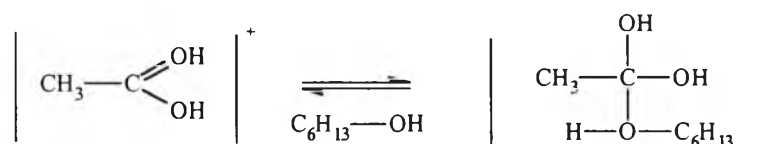
## 2.4 Esterification reaction

Esters can be prepared by esterification of an acid with an alcohol in the presence of an acid catalyst (sulfuric acid, hydrochloric acid).[8] The mechanism involve the following :

### (1) Protonation of the carboxyl group



### (2) Addition of the alcohol



### (3) Elimination of water and deprotonation



Since the reaction is reversible , the equilibrium must be shifted forward to obtain good conversion to the esters by use of an excess of one of the initial

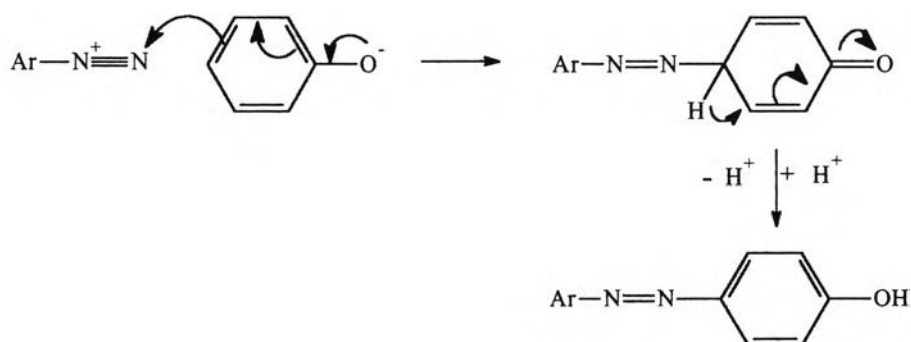
reactants, and removal of the water by distilling off a water-alcohol azeotrope to complete esterification reaction.

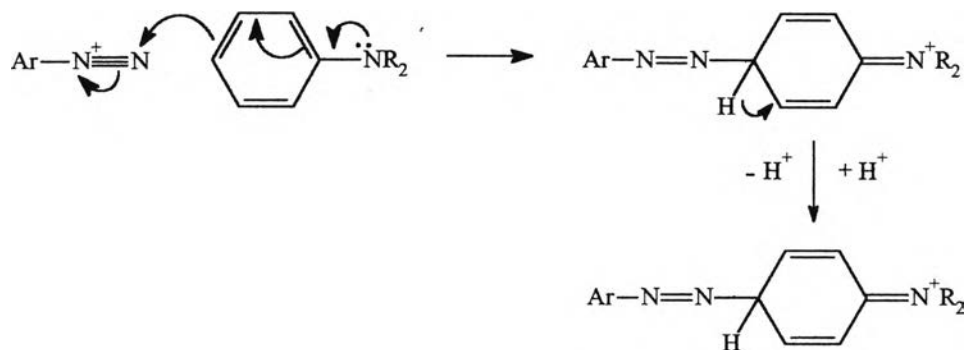
Hydrolysis of an ester is the reverse of esterification by strong alkalies, saponification.[9]



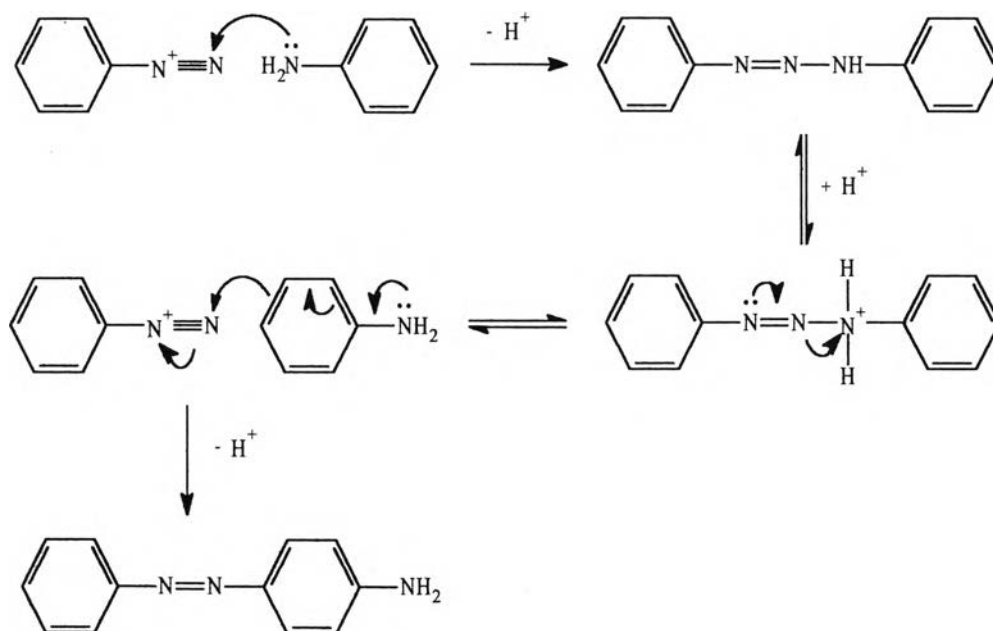
## 2.5 The coupling reaction of the azo dye

Azo dye compounds are synthesized by the interaction of a diazonium salt with phenol in the presence of sodium / potassium hydroxide or with an amine and sodium nitrite in the presence of acidic condition.[10,11,12] The coupling reaction is an electrophilic substitution involving the diazonium ion, which react at the position of greatest electron availability, such the ortho or para position can be release electron to phenoxy or amino groups. Coupling reaction never occure at the meta position if para and ortho position are occupied.





The coupling reaction occurs between the diazonium salt and the amino group in the amino to yield the diazoamino compounds or phenol group in the phenoxy to yield diazophenoxy compounds. Thus diazoaminobenzene prepared by dissolving aniline in the presence hydrochloric acid, and adding sodium nitrite in aqueous solution by the following scheme.[13]

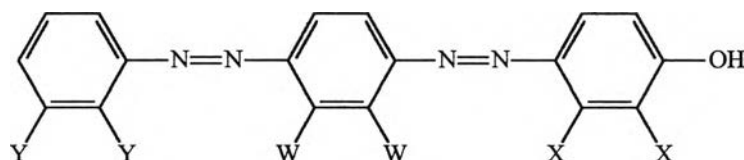


## LITERATURE REVIEWS

US Patent No. 5252106 "Base Extractable Petroleum Marker"[2]

Hallisy, M. J., Oct.12,1993.

Liquid petroleum products are marked with markers having the formula :



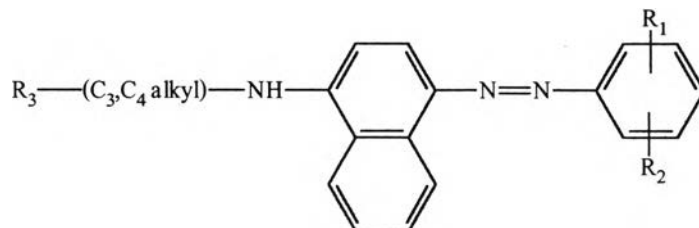
Where the Ws are selected from O—(C1-C3 alkyl) and hydrogen, provided that the Xs and Ys are the same or different and are select form hydrogen, alkyl, substituted alkyl, alkenyl, substituted alkenyl, aryl, substituted aryl, fuse aryl, substituted fuse aryl, halogen, nitro, cyano and alkoxy.

These markers are conveniently synthesis by azo coupling of appropriate aniline to a phenol such as 2,6-di-sec-butyl phenol . It is added into fuel in a level of 5-40 ppm. The markers may be detected by shaking with alkaline extraction solution, for example 1-3% of NaOH or KOH and the quantity amount of marker is determined in aqueous phase by colorimetric equipment.

US Patent 5490782 "Acid extractable petroleum fuel markers"[3]

Friswiell, R., Hallisy, J. and Hinton, M.P, Feb. 13, 1996

Petroleum fuels are marked with markers having the general formula :



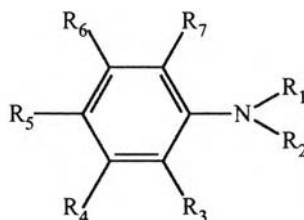
Where  $R_1$  and  $R_2$  are selected from hydrogen, methyl, ethyl, methoxy, halogen, cyano and nitro and  $R_3$  is selected from methyl, methoxy, methoxyethoxy and morpholino.

Markers of this patent are synthesized by azo coupling of substituted aniline to an alpha-naphthylaniline. They are generally, colorless or have a pale yellow color at level 5-40 ppm. The markers were extracted by 10% HCl, formic acid and phosphoric acid aqueous solution, giving a detectable color in aqueous phase.

US Patent 5627077 "Aniline as markers for mineral oils"[15]

Rainer D. B., Friedrich W. R., May. 6, 1997.

Aniline of the formula:



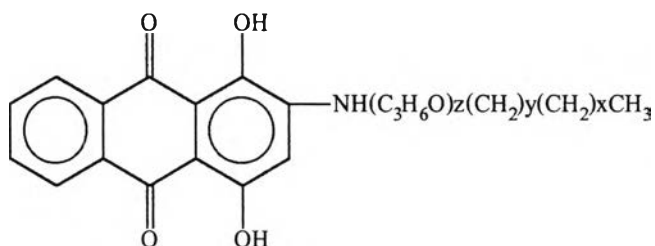


Where  $R_1, R_2$  are each hydrogen, C1-C18-alkyl. The aniline derivatives are used as marker in mineral oil and extracted by treating with aqueous solution of diazonium salt of 1-amino anthraquinone or 2-chloro-4-nitroaniline. The mixture is shaken with inorganic or organic acid, such as hydrochloric acid, sulfuric acid, citric acid and orthophosphoric acid. The color of the aqueous phase is differed by changing the of aniline and diazonium salt and can be quantified by measure absorbance of aqueous phase.

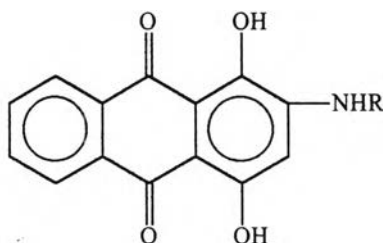
US Patent 4764474 “Method for detecting a tagging compound”[16]

Orelup, R.B., Aug.16,1988.

Tagging compounds having the following formula :



or

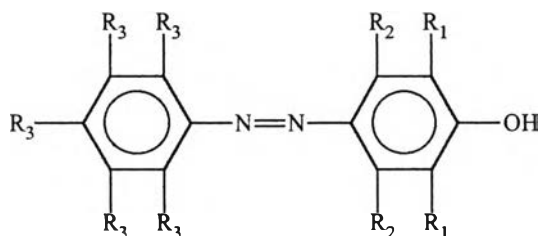


Where X is an integer between 0 and 3 inclusive , Y is an integer between 1 and 3 inclusive, Z is 0 or 1, and R is a straight or branched chain hydrocarbon having from 1 to 5 carbon atoms are disclosed. The alkalines are used as an extraction solvent. The reagent settles to the bottom and is colored if marked fuel is present. The amounts of markers can be determined by measuring absorbance of the colored solution instrumentally and related to marker concentration.

US Patent 516653 "Silent markers for petroleum, method of tagging, and method of detection" [7]

Friswell, R.; and Orelup R.B., Oct. 20, 1992.

Liquid petroleum products are marked with markers having the following formula :

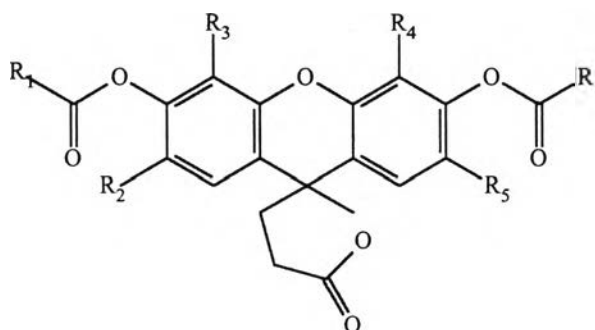


Where the  $R_1$  and  $R_2$  are each selected from hydrogen and C1-C7 alkyls .  $R_3$ s are selected from -H, -NO<sub>2</sub>, -Cl, -Br, -F, -CN and -Me. These marker compounds are synthesized by azo coupling of an aniline to a 2,6-dibutyl phenol. The marker may be detected by extraction with a reagent comprising water and measurement of absorbance of aqueous solution is used to determine the amount of marker in fuel.

US Patent 5498808 "Fluorescent Petroleum Markers"[17]

Smith, M.J. Mar.12,1996.

The marker having formula :



Where R1 is an alkyl or aryl. R2, R3, R4, R5 are -H, -Cl, -Br or C1-C12 alkyl.

Compositions of the markers contain organic esters of fluorescent of Xanthene dyes, which may be added to fuels, lube oil and greases, but they are colorless in petroleum products, their presence is detected by reacting them with a developing agent. Tagging fuel shaken with extraction media, for example, a mixture of water, aliphatic alcohols, glycols, glycol ethers or quaternary ammonium hydroxide compound. The amounts of marker may be detected in aqueous phase by spectrofluorometer.