

## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 The cashew tree and Cashew Nut Shell Liquid (CNSL) [6]

The cashew tree, *Anacardium occidentale* Linn., is a native of Brazil and was introduced into Asia and Africa by the portuguese in the 1,600's. It is now found widely in other parts of tropical zones. It is a jungle or semi-jungle tree by native. The cashew nut is grey-brown in color and shaped like the kidney. The shell of the nut is hard and consists of two layers (see the figure 2.1). The outer layer is smooth surfaced, thin and tough. But the inner layer is hard. Between of the two layers is a honeycomb structure which contains a phenolic material known as "Cashew Nut Shell Liquid (CNSL)". Inside the shell is the kernel wrapped in a thin brown skin, known as the testa.

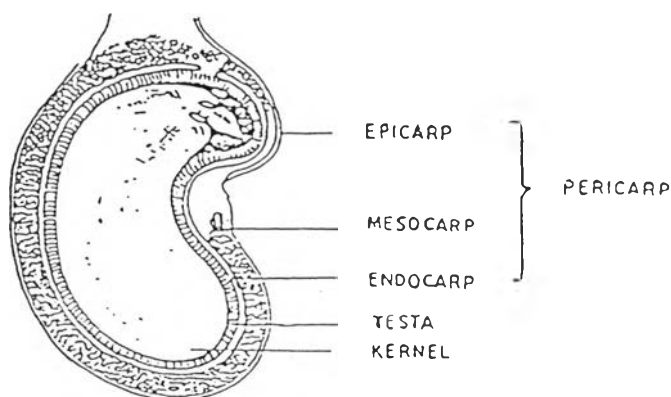
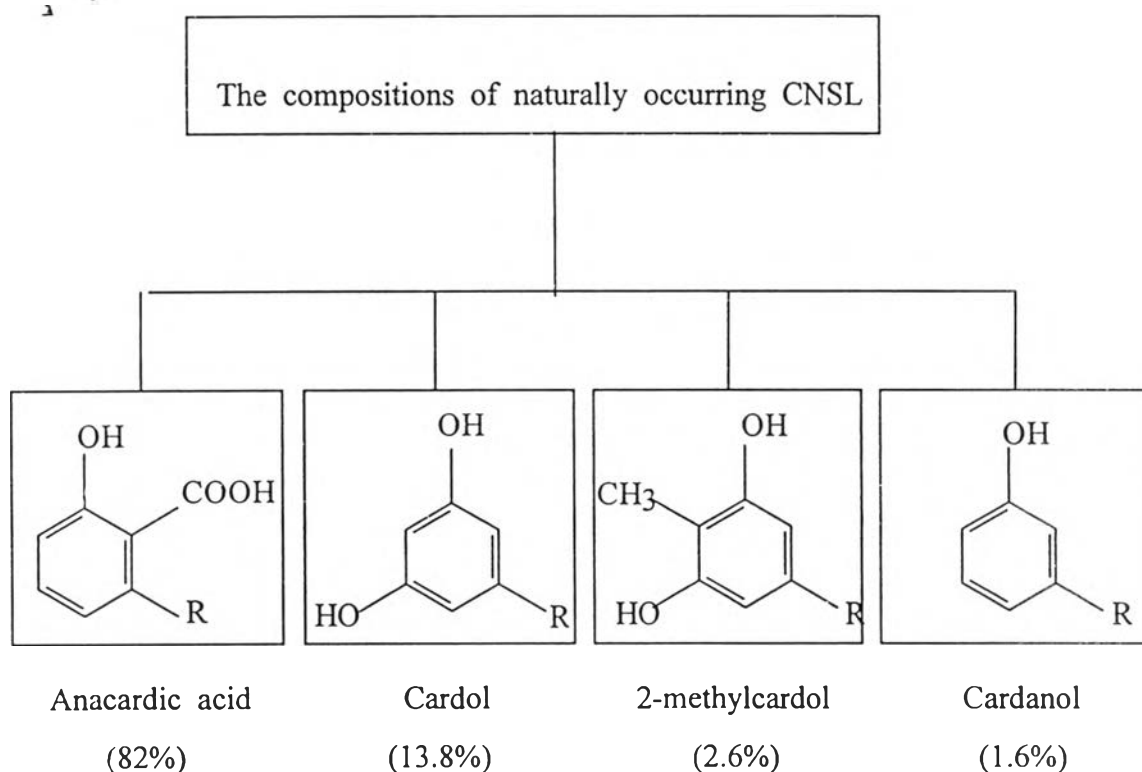


Figure 2.1 : The section of a cashew nut.

The cashew nut shell liquid is contained between the soft outer skin of the nut and the harder inner shell. It is dark brown viscous liquid which can be extracted by the organic solvents such as n-hexane. This method enables 85 to 90 per cent of the CNSL to be recovered. The principal components of the CNSL are the derivatives of 6-pentadecylsalicylic acid (anacardic acid), 5-pentadecylresorcinol (cardol), 2-methyl-5-pentadecylresorcinol (2-methylcardol) and 3-pentadecylphenol (cardanol), which differ in their types of C<sub>15</sub> side chains (saturated, monoene, diene, and triene).[7]



R = -(C<sub>15</sub>H<sub>25-31</sub>)

: -(CH<sub>2</sub>)<sub>14</sub>CH<sub>3</sub>

-(CH<sub>2</sub>)<sub>7</sub>CH=CH(CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>

-(CH<sub>2</sub>)<sub>7</sub>CH=CHCH<sub>2</sub>CH=CH(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>

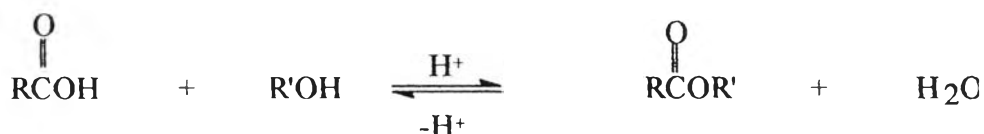
-(CH<sub>2</sub>)<sub>7</sub>CH=CHCH<sub>2</sub>CH=CHCH<sub>2</sub>CH=CH<sub>2</sub>

Anacardic acid readily loses carbon dioxide to yield a meta-substituted phenol (Cardanol) on heating. During the commercial processes, the CNSL is held at the high temperature for several hours. Considerable decarboxylation of the anacardic acid takes place, as well as some polymerization of the phenolic bodies to yield a commercial CNSL, which is mainly monophenolic in character. But it contains a small amount of anacardic acid (approximately 16%), cardol and polymerized material. [8]

The sources of the cashew nut in Thailand are mainly in the South and the Northeast. The CNSL is the raw material used in varnish materials, lacquer, printing ink, phenolic resins, dyes, paints, lubricating substances, electrical insulation, rubber-like compositions, insecticide compositions, brake materials, filter material, adhesive and coating compositions, medicine compositions, photosensitive compositions and gaskets, etc. [9] The CNSL is available at large quantities because it is the by-products in those commercial processes. Moreover, it contains the mixture of phenolic compounds that can be coupled with the diazonium salts of chloronitroaniline derivatives to be used as the marker dyes. So it is reasonable to make use of this raw material for synthesizing the marker dyes.

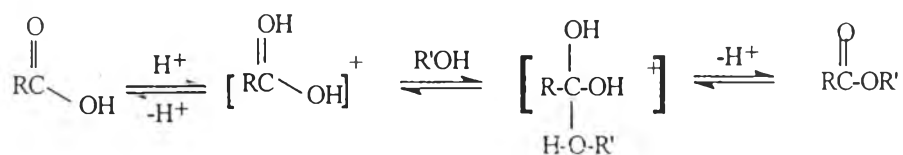
## 2.2 The esterification

The esters may be provided by direct esterification. The reactants are acid and alcohol in the presence of acid catalyst such as sulfuric acid following this reaction :



The esterification involves this following mechanism :

- Protonation of the carboxyl group
- Addition of alcohol
- Elimination of water and deprotonation



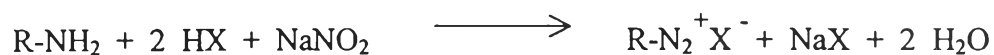
This reaction is achieved by using two-fold of the acid catalyst. The removal of water and the excess of reactants should be completed by adding toluene and distilling out a ternary azeotropic mixture, toluene-alcohol-water.

[10]

### 2.3 Synthesis of Azo Dyes

Azo dyes are from the largest and most versatile class of all dyes. They are a well-defined group of compounds characterized by the presence of one or more azo groups (-N=N-). Azo dye chemistry involves two basic reactions; diazotization and coupling reaction. [11]

#### 2.3.1 Diazotization



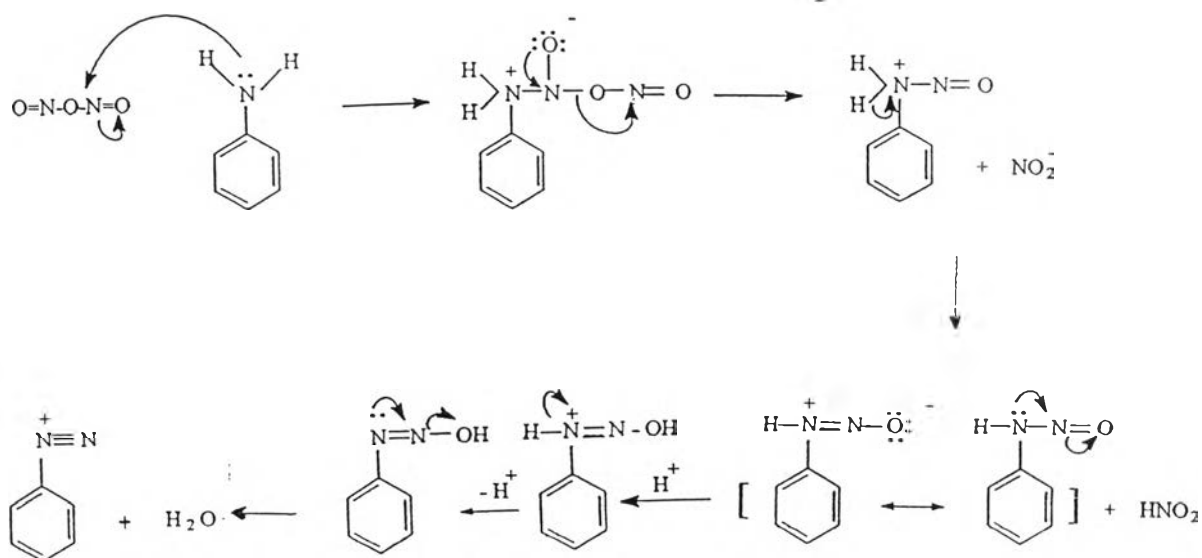
Where X equals  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ ,  $\text{HSO}_4^-$ ,  $\text{BF}_4^-$ , etc.

While the nitrite must be used in exactly the amount theoretically required 2 equivalents. The excess of acid must be increased to 1 to 3 equivalents in diazotizations of weakly basic amines whose salts are readily hydrolyzed such as chloro- and nitroanilines. [12]

The solutions of diazonium salts are prepared by dissolving the amine compound in dilute acid, cooling to 0-5°C and adding gradually with stirring. The dilute sodium nitrite are cooked until the mixture turns the starch-iodide paper blue. The reaction mixture must be kept very cold during the processes. [13]

It was found that the speed of diazotization is a function of the kind and concentration of acid employed rather than of the hydrogen-ion concentration. The diazotization proceeded least rapidly in nitric, sulfuric acid, more rapidly in hydrochloric acid and most rapidly in hydrobromic acid. [15]

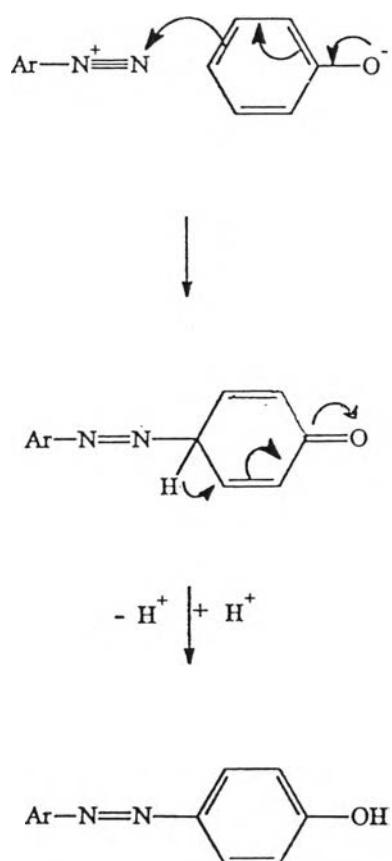
The mechanisms of the diazotization are the following equations: [14]



### 2.3.2 The azo coupling reaction

The diazonium salts undergo reactions with highly reactive aromatic compounds such as phenols or amines. This coupling reaction is an electrophilic substitution at the reactive para or ortho positions of phenols or amines. If the para-position is blocked, the coupling reaction occurs in the ortho-position. However, the coupling reaction will not occur if para- and ortho- position are blocked. It was found that the coupling reaction cannot react at meta- position. [16]

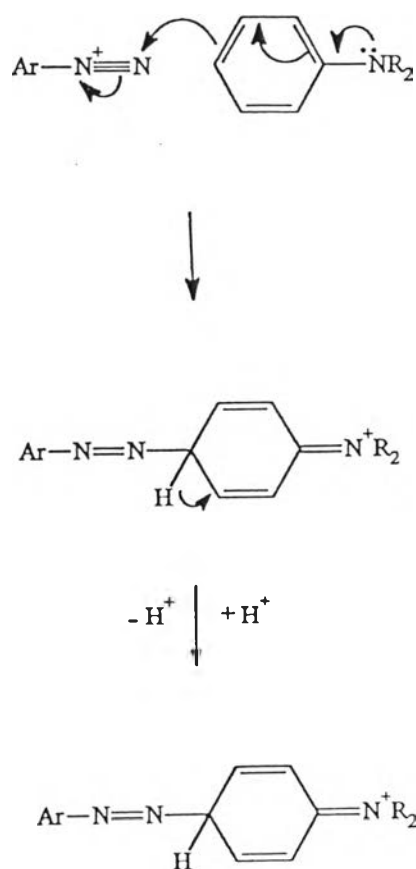
When the coupling components are the highly reactive phenols, The mechanisms will be occurred :



Control of pH is important for this reaction. The diazonium group is not a powerful electrophile and will not react with phenol. Instead, the conditions must be sufficiently basic to convert the phenol to phenolate ion which reacts rapidly. In the practice, the coupling reaction with phenols is usually carried out at pH 5 to 9.

In acidic solution, an amine is largely in the unreactive ammonium salt form, since the coupling reaction will occur with free amine, the solution must be made more basic than is necessary for diazotization. A pH range of 3.5 to 7 is usually chosen in practice. [17]

When the coupling components are the highly reactive amines, the mechanisms will be occurred :



## 2.4 Marker dyes for petroleum fuels

Marker dyes are the combination of the important characteristics of markers and dyes. A dye is defined herein as a material lending visible color when dissolved in the dyed products. In case of a marker, it is defined herein as a substance which can be dissolved in a liquid to be identified and then detected by performing a simple chemical or physical test on the tagged liquid. [5]

So, the important characteristics of novel marker dyes for petroleum fuels include :

1. They can be supplied as liquids having high solubility in petroleum fuels.
2. They do not alter the appearances of petroleum fuels to which added.
3. They can not be easily proved their chemical structures and removed from petroleum fuels without the appropriate methods.
4. They can be identified by the detection procedures (the field tests) and the quantitative determinations (the laboratory methods).
5. They should have high storage stability in petroleum fuels.

The amount of marker dyes in petroleum fuels is usually proposed to have about 5-40 ppm, enabling the marker dye to be detected. [4] The one choice of the simple field test should be the solvent extraction system because this method is sophisticated by the availability of testing equipment and it may be possible to use less marker dye. Furthermore, it is a quick one step test that can be provided the simple quantitative determinations.



The solvent extraction system comprises between about 10 to 60 volume percent of water, 10 to 60 volume percent of water-soluble amine and up to about 60 volume percent of a cosolvent which is miscible in aqueous media and substantially immiscible in petroleum fuels. In case of cosolvents, the oxygenated substances are miscible with water and immiscible with the petroleum fuels. They have significantly advantageous effects with shade, the intensity of the developed color and the degree of interference from fuel components. If the developed color is stable, the relative quantitative determinations of marker level will be facilitated. The suitable cosolvents include alcohols, glycols and glycerine.

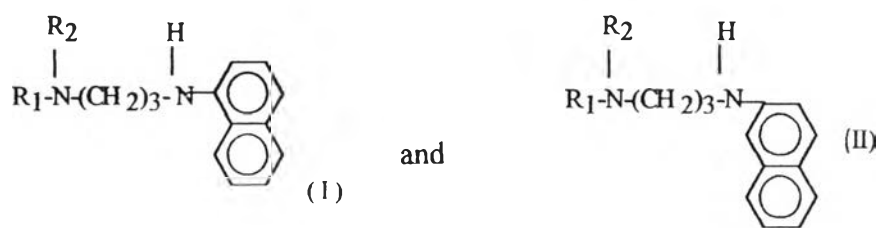
In the simple field test, the volume ratio of petroleum fuel to the solvent extraction phase is between 1:1 and about 1:10. If the marker is present in the petroleum fuel, it will be extracted by the aqueous layer and colored by reaction with the extraction mixture. [5]

## 2.5 The literature reviews

The synthetic marker dyes were mentioned in these literatures following below :

U.S. patent 4209302 : Marker for petroleum fuels (1980) [4]

These markers include the following compounds:

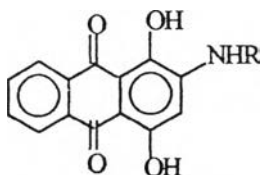


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Where  $R_1$  and  $R_2$  may be hydrogen or alkyl having from 1 to 20 carbon atoms or morpholine group. The marker is added to the fuel about 12 parts per million. It imparts no coloration to the fuel. If the R group is the morpholine group, The marker (I) will be detected by extraction with an acidic aqueous solution such as methane sulfonic acid or hydrochloric acid. Then a stabilized solution of diazotized 2-chloro-4-nitroaniline is added to yield an intense bluish pink color. In case of marker II, a weak yellow color will appear after addition of the diazotized 2-chloro-4-nitroaniline to the acidic aqueous extract.

U.S. patent 4735631 : Colored petroleum markers. (1988) [18]

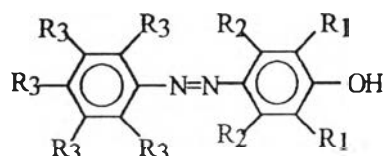
Tagging compounds which functions as both dyes and markers having the following structures:



Where R is a straight or branched chain hydrocarbon. The marker is added to the fuel from about 1 to 15 parts per million. Then the sample of fuel (20-50 ml) suspected to contain tagged fuel is shaken with approximately 1:10 its volume (2 to 5 ml) of the reagent which comprises with glycerine, water and an organic amine. The reagent settles to the bottom and is colored bluish red if marked fuel is present. If the sample contains no marker, the reagent layer remains colorless or very slightly yellow for some fuels.

U.S. patent 5156653: Silent markers for petroleum, method of tagging and method of detection. (1992) [3]

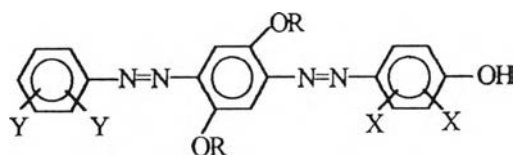
The liquid petroleum fuels are marked with markers having the formula :



Where  $R_1$  and  $R_2$  are the same or different from -H or  $C_3$ - $C_7$  alkyls at least one and  $R_3$  are the same or different from -H,  $-NO_2$ , -Cl, -Br, -F, -CN at least one. The marker is detected by the solution of water, water-soluble amine and water-miscible cosolvent such as alcohols, glycerols or esters. A deep color can be developed in the aqueous phase with red to blue shade. The maximum absorbance is measured to compare the presence of marker level in petroleum fuels.

U.S. patent 5252106: Base extractable petroleum markers. (1993) [5]

The marker of the general class of phenylazophenols having the formulas:

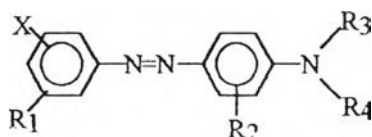


Where preferably X are alkyl, alkenyl, aryl and their substitutions and preferably Y are electron withdrawing such as halogen, nitro and cyano. It is generally necessary to have 5-40 ppm in the petroleum fuels, enabling the marker to be detected. It is detected by extraction with NaOH in aqueous

methanol. A deep color of green-blue-gray-black shade will developed in the aqueous layer.

U.S. patent 5266227: Oil-soluble phenylazoaniline dyes.(1993) [19]

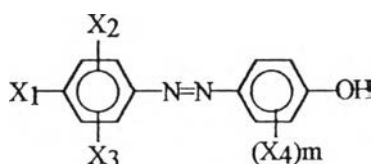
Azo dyes useful for marking mineral oils have the formula:



Where  $R_1, R_2$  are  $-H, C_1-C_4$  alkyl or  $C_1-C_4$  alkoxy and  $R_3, R_4$  are  $C_1-C_8$  alkyl which may be substituted by hydroxyl. X is cyano or substituted or unsubstituted  $C_1-C_8$  alkoxy carbonyl. The 10 ml of marker in unleaded motor gasoline was examined by shaking with a mixture of hydrochloric acid and ethanol. The alcoholic aqueous phase turned visibly red after standing for a short time. The red layer was colormetrically compared against a solution of known concentration to obtain a quantitative determinations of dye content.

U.S patent 5487770 : Detection of marked mineral oils and novel azo dyes. (1996) [20]

An azo dye of the formula:



Where  $X_1$  is  $-H, C_1-C_4$  alkyl, cyano or nitro,

$X_2$  is  $-H, C_1-C_4$  alkyl, cyano or nitro,  $C_1-C_4$  alkoxy or  $C_1-C_{16}$  alkoxy carbonyl,

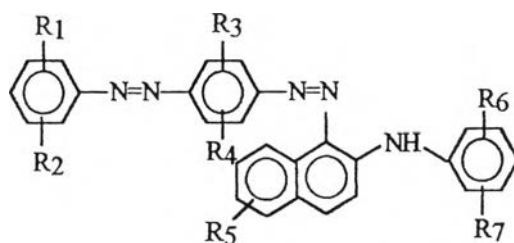
$X_3$  is -H,  $C_1$ - $C_4$  alkyl, cyano or  $C_1$ - $C_{16}$  alkoxy carbonyl, and

$X_4$  is -H, hydroxyl, substituted or unsubstituted  $C_1$ - $C_8$  alkyl.

Method for detecting marked mineral oils by treating the marked mineral oils with an solvent extractant comprising a partially or completely water-miscible organic solvent, and as base an alkali or alkaline earth metal hydroxide, an alkali metal carbonate or a quaternary ammonium hydroxide. In course of the treatment of the marked mineral oil with the extractant, for example by shaking, the azo dye of the above formula transfer into the aqueous phase, which takes on a distinctly visible color on yellow to strongly orange.

U.S. patent 4049393: Colored petroleum derived – products. (1977) [21]

The novel disazo colorants or dyes for marking organic liquids having the general formula :

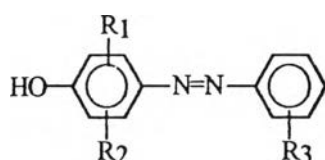


Where  $R_1$  and  $R_2$  are H or alkyl having from 1 to 4 carbon atoms,  $R_3$  and  $R_4$  are each H,  $OCH_3$ , or  $CH_3$  and  $R_5$ ,  $R_6$ , and  $R_7$  are each H or alkyl having from 1 to 12 carbon atoms. These colorants display a surprisingly high solubility in all water – immiscible organic liquids. A concentration of 20 parts

per million of colorants was chosen to be added to petroleum product to achieve 100% marked product. A visual “on-the-spot” field test is provided by shaking the marked fuel with 1 or 2 grams of an adsorbent such as a clay or a preferably hydrated silica. The mixture is allowed to settle to form a clear upper layer and a sediment, whereupon the color of the clear fuel becomes visible and color bodies naturally present in the fuel are removed by the adsorbent. The simple quantitative test is possible to detect the color of the disazo colorant where the 100% marked fuel has been diluted. The clear layer is separated from the sediment by filtration. The absorbance of the filtrate is measured at the specific wavelength.

Marker dyes from cashew nut shell extract and nitroanilines. [23]

The marker dyes include the following compounds :

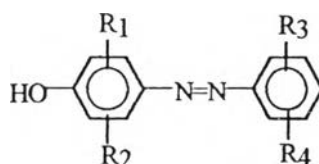


Where  $R_1$  is H or  $\text{COOC}_6\text{H}_{13}$ ,  $R_2$  is  $\text{C}_{15}\text{H}_{25-31}$ , and  $R_3$  is  $-\text{NO}_2$  group. The starting phenol ester is from the esterified cashew nut shell liquid (CNSL) consisting of the mixtures of phenolic compounds. The 15 ppm of these marker dyes are added into the liquid petroleum fuels. The method for detecting dyed petroleum fuels is achieved by treating with an solvent extractant comprising 5% wt. potassium hydroxide in ethylene glycol. In course of the treatment of the dyed petroleum fuels with this extractant, the marker dyes of the above formula transfer into the aqueous phase and takes yellow,

orange and red color when  $R_3$  is o-nitro, m-nitro and p-nitroaniline, respectively. The quantitative analysis is measured by UV-VIS spectroscopy technique. The storage period of dyed petroleum fuels has no effect on the quality of marker levels after 3 months.

Marker dyes from cashew nut shell extract and chloroanilines.[24]

The liquid petroleum fuels are tagged with the following compounds :



Where  $R_1$  is H or  $\text{COOC}_6\text{H}_{13}$ ,  $R_2$  is  $\text{C}_{15}\text{H}_{25-31}$ , and  $R_3, R_4$  is Cl- group.

The starting phenol ester is from the esterified cashew nut shell liquid (CNSL) comprising of the mixtures of phenolic compounds. It is reacted with chloro- or dichloroaniline by the coupling reactions. The 200 ppm of these marker dyes in liquid petroleum fuels are examined by shaking with an extractant consisting of 10% wt. potassium hydroxide in methanol. The aqueous phase turns visibly yellow color after standing for a short time. The determination of marker levels is achieved by UV-VIS spectroscopic technique.