CHAPTER II
THEORY AND LITERATURE REVIEW

2.1 Colors and UV/VIS spectroscopy [8, 9, 10, 11]

The absorption of ultraviolet or visible light, which ranges from 100 – 750 nanometer (nm) are generally occurred by organic or complex compounds having color or not. It is used as a method for qualitative and quantitative analysis of chemical compounds. Typically, this technique is called "UV/VIS spectrophotometry", but if the sample is colored or can make color, it may be called "Colorimetry".
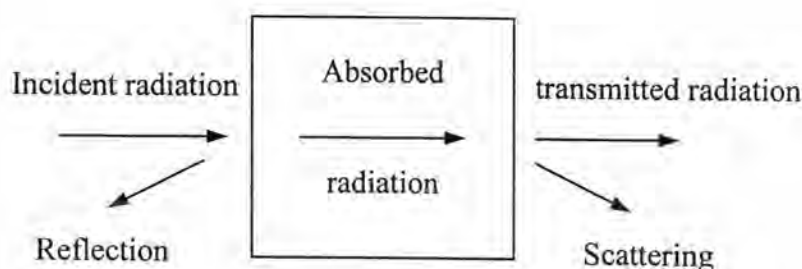

Figure 2.1 Interaction of chemical compound with light or radiation.

When a continuous beam of light passes through a chemical compound, one part of the light is reflected, one part is absorbed, one part is scattered, and another part is transmitted. This last part lacks those portions of the incident light that have been absorbed or reflected, and their absence will reveal on their own spectroanalytically in absorption bands. Since the reflected light has a different composition from the incident light, selective absorption of certain wavelengths of the spectrum has occurred. Whenever selective absorption occur in the visible part of the spectrum, the eye will perceive the change as an appearance of the complementary color to the colors represented by the absorbed wavelengths. The range of wavelengths, color of the corresponding light beam, and complementary colors of the various regions of the spectrum are given in Table 2.1.

Table 2.1 Colors in the visible spectrum

Wavelength, nm	Colors	Complementary color
400-425	Violet	Greenish-yellow
425-450	Indigo	Yellow
450-510	Blue	Orange
510-550	Green	Red
550-590	Yellow	Violet
590-640	Orange	Blue
640-700	Red	Green

Since white light confers different colors on different chemical compounds, it is clear that the reason for this must be found in the different chemical constitution of these bodies. Hence color is a function of the chemical constitution of the molecule. In 1876, Witt observed that some types of organic structures gave rise to color, while others did not. The partial structures necessary for color were called *chromophores.* There were 3 groups of simple chromophores, which were:

1.Chromophores having multiple bonds between 2 atoms, which did not have a lone pair of electron, such as $C=C$

2.Chromophores having multiple bonds between 2 atoms, which one atom has a lone pair of electron, such as

$$C=O$$

3.Chromophores having a benzene ring, i.e. aromatic hydrocarbon compound.

If themselves or others conjugate these chromophores, the new absorption band will occur. This usually shifts the absorption into the longer wavelength.

Some other groups, which do not absorb UV-VIS light or slightly absorb the light result in an absorption spectrum of chromophores, called *auxochromes.* The effects of auxochromes to the absorption of chromophores include:

1.Bathochromic shift (red shift), the absorption spectrum was changed into a longer wavelength, λ_{max} was increased.

2.Hypsochromic shift (blue shift), the absorption spectrum was changed into a shorter wavelength, λ_{max} was decreased.

3.Hyperchromic effect, the intensity of absorption spectrum was increased:

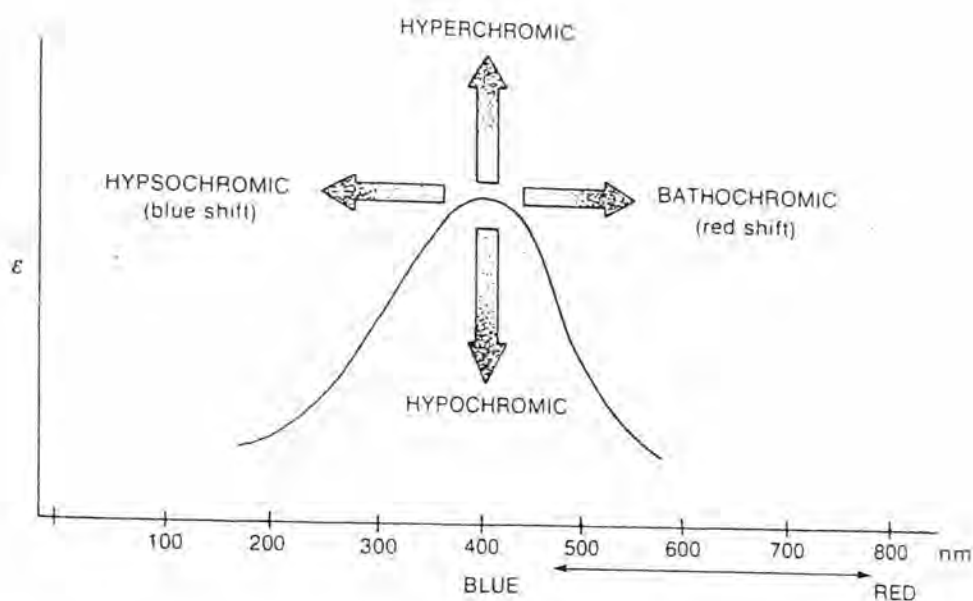4.Hypochromic effect, the intensity of absorption spectrum was decreased.

Figure 2.2 Effect of auxochrome to absorption of chromophore

A UV-VIS spectrophotometer is designed in order that the absorption of a sample is measured at various wavelengths and plotted by a recorder to give the spectrum. The wavelength of absorption is usually reported as the maximum wavelength (λ_{max}), which is the wavelength at the highest point of the curve, while the absorption of energy is recorded as absorbance. This is shown below in the equation of Beer's law.

$$A = \varepsilon bc$$

Where A = absorbance

ε = molar absorptivity

b = cell length, in cm

c = concentration, in mole/litre

It is found that the absorbance of solution is directly proportional to the concentration. This relation is advantageous due to the quantitative analysis using a

standard calibration curve, which is produced by measuring absorbance at a maximum wavelength of standard solution at various concentrations. The standard calibration curve is a plot between absorbance and the concentration of standard solution, which is shown in Figure 2.3. When the absorbance of a sample is measured, the quantity of the sample is obtained by comparing the absorbance with a standard calibration curve. The absorption spectrum of sample is also shown in Figure 2.4.
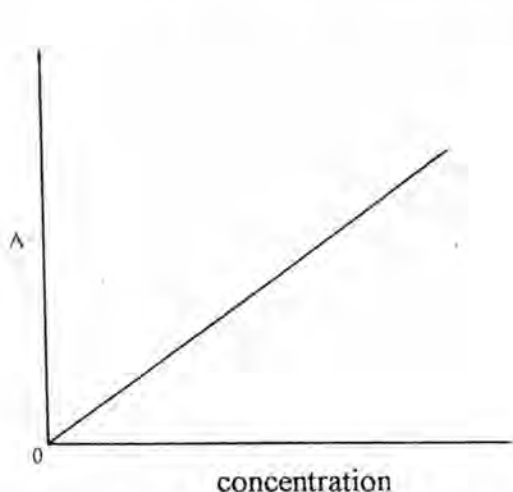

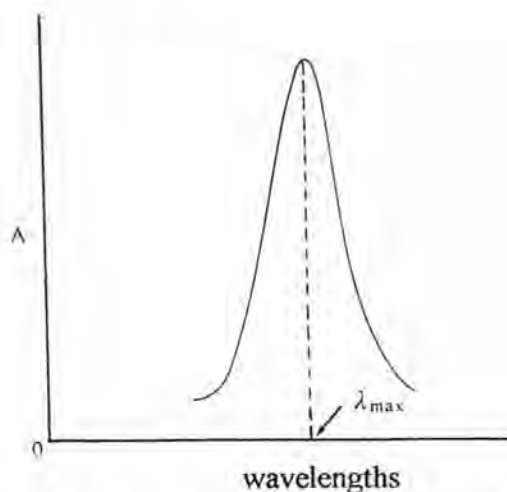**Figure 2.3** The standard calibration curve of solution

Figure 2.4 The absorption spectrum of sample

2.2 Markers [3]

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. The important characteristics of desirable markers for petroleum products include:

1. They are entirely foreign to the liquid.

2. They can be supplied as highly concentrated solutions in petroleum-compatible solvent.

3. They are easily detected by unstable natural components of the liquids.

4. They are not obscured by unstable natural components of the liquids.

5. They are stable over the anticipated storage life of the tagged liquid (usually three to six months).

6. They have identities, which can be confirmed by laboratory methods.

Moreover, the markers should provide substantially no color in the petroleum products, but undergo a reaction during a detection procedure. Extraction by a petroleum-immiscible solution is a detection procedure, which can transfer the marker from a petroleum product to extraction solution and develops a color, which is sufficiently different from the background color.

2.3 Azo dyes [8, 11, 12]

Dyes are colored organic compounds that are used to impart color to the object such as fabrics and petroleum products. Azo dyes are the largest and most important class of dyestuffs, which have been added to petroleum products for marking.

The general formula of azo compound is Ar-N=N-Ar' which is prepared by coupling a diazotized aromatic amine with a aromatic ring containing a powerfully electron-releasing group, generally –OH, -NR$_2$, -NHR, or –NH$_2$. The diazotized aromatic amine or diazonium salt is formed by a diazotization reaction, a primary aromatic amine which is dissolved or suspended in cold aqueous mineral acid is treated with sodium nitrite. Diazonium salt is used immediately after preparation because it slowly decomposes even at ice-bath temperatures.

$$ArNH_2 \;+\; NaNO_2 \;+\; 2\,HX \xrightarrow{\text{cold}} ArN\equiv N^+X^- \;+\; NaX \;+\; 2\,H_2O$$

1°aromatic amine   Diazonium salt
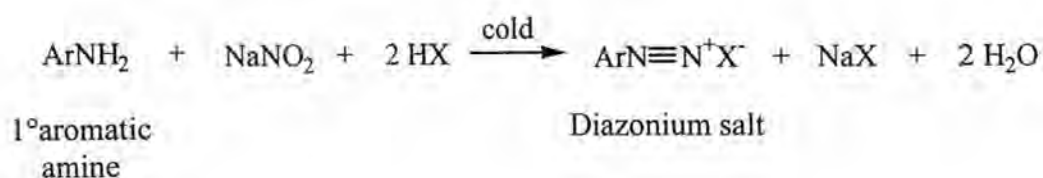
Coupling is an electrophilic aromatic substitution in which the diazonium ion is the attacking reagent. Substitution usually occurs para to the activating group.
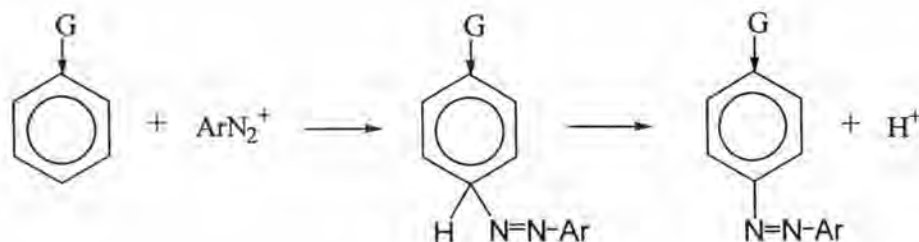
Coupling with phenols, in general, is carried out in a mild alkaline solution, and with amine in a mild acidic solution. It is most important that the coupling medium be adjusted to the right degree of acidity or alkalinity by the addition of the proper amount of hydroxide or salt like sodium acetate or sodium carbonate.

Azo dyes can change color with a change in pH, like an acid-base indicator, because the chromophoric system is changed by acid-base reaction. For instance, in an acidic solution, methyl orange exists as a resonance hybrid of a protonated azo structure; this resonance hybrid is red. The azo nitrogen is not strongly basic, and the protonated azo group loses the hydrogen ion at about pH 4.4. The loss of the proton changes the electronic structure of the compound resulting in a change of color from red to yellow. As a result, azo dyes are good markers in fuel oils, which can be detected easily by extraction with simple acid or basic solution.

Methyl orange

(yellow in base)
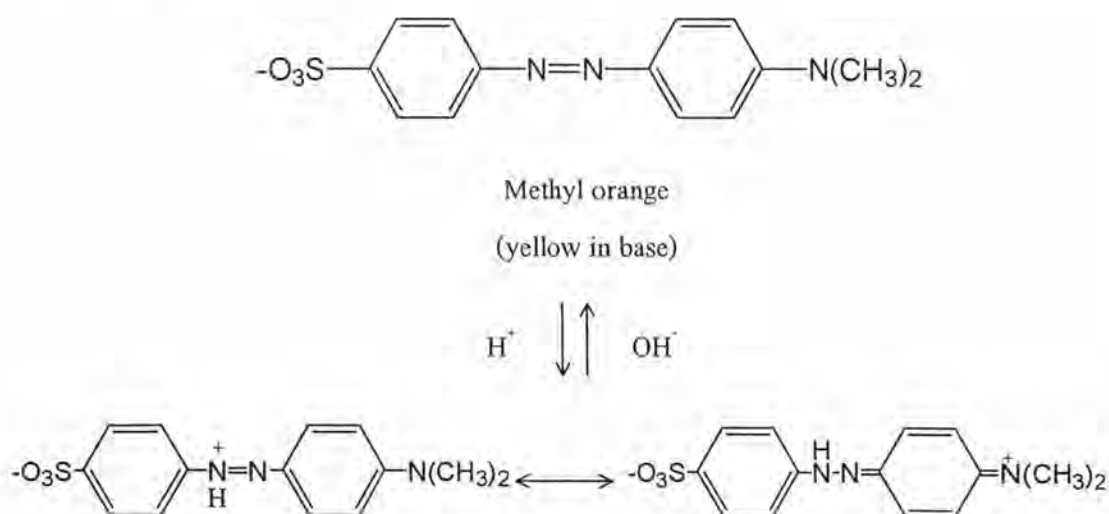
2.4 Linear alkylbenzene [7, 13]

Linear alkylbenzene is made by alkylating benzene with n-olefins, which are manufactured from n-paraffin in one of four industrial processes: by thermal cracking, chlorination and dehydrochlorination, dehydrogenation, or by Ziegler oligomerization of ethylene. Depending on the source, the n-olefins used may be essentially dodecene, or may be a mixture spanning the range C_{10} to C_{14}. To obtain high selectivity to the linear mono olefins, the paraffin's are usually incompletely reacted. The resulting paraffin/olefin mixture can be directly used for benzene alkylations because the distillation of the alkylation's mixtures is simpler than the separation of the paraffin/olefin mixture. Alkylations of benzene with n-olefins are generally done in the liquid phase at temperatures in the range 40-70°C with HF, HBF_4 or $AlCl_3$, but it is also done in the gas phase. A large excess of benzene is used to suppress polyalkylation.

Furthermore, linear alkylbenzene is made by alkylating benzene with chloroalkanes, which is carried out in the $AlCl_3$ at temperatures in the range 40-85°C. The yield is rather lower than in the alkenes-based processes. However, this lower yield is counterbalanced by the fact that the alkenes-based process involves the handling of large amounts of hydrogen fluoride, a rather than hazardous material.

Currently, linear alkylbenzene is used for the manufacture of alkylbenzenesulfonate for cleaning agents in many countries throughout the world. The production capacity for linear alkylbenzene in Western Europe, the USA, and Japan is given in Table 2.2

Table 2.2 Production of linear alkylbenzene (in 1,000 tones)

Countries	Years			
	1998	1990	1994	1995
W. Europe	508	524	485	530
USA	166	173	180[*]	380
Japan	197	212	197	150

[*]1991 [7]

2.5 Nitration reaction [14, 15, 16]

Nitration means the introduction of the nitro group, -NO$_2$, into a molecule. It is accomplished: (1) with dilute or concentrated nitric acid; (2) with mixed acid, i.e., a mixture of nitric and sulfuric acid, sometimes containing some water; (3) by first sulfonating the compound and then nitrating the sulfonic acid, thereby splitting out the sulfo group and replacing it by the nitro group; (4) by oxidizing with dilute nitric acid a previously formed nitroso compound; and (5) by treatment of a diazonium compound with hot, dilute nitric acid, introducing simultaneously a hydroxyl group and nitro group.

Nitration of aromatic compound is carried out industrially using a mixture of nitric and sulfuric acids (mixed acid or nitrating acid). The function of the sulfuric acid is to convert the nitric acid into the highly reactive, electrophilic, nitronium ion, $^+$NO$_2$, which is the effective nitrating agent. The sulfuric acid is also an excellent

$$ArH + HNO_3 / H_2SO_4 \longrightarrow ArNO_2$$

$$HONO_2 + H_2SO_4 \longrightarrow {}^+NO_2 + H_3O^+ + 2\,HSO_4^-$$
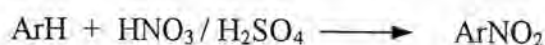
solvent for many substances. Due to its high heat capacity, the sulfuric acid serves to absorb the heat of reaction, producing a smooth and uniform reaction. Since nitration is a strong exothermic reaction, good cooling should be provided. Generally, many nitrations go smoothly only at lower temperatures because oxidation or some other side reactions may be strongly favored at higher temperatures. In addition, it is absolutely necessary to have continuous vigorous stirring in all nitrations especially if the substance being nitrated does not dissolve in the nitric acid. Because if no stirring is used, two layers are formed and when the reaction starts at the liquid-liquid interface, strong local overheating occurs which might lead to an explosion.

Nitration of linear alkylbenzene gives a mixture of products because an alkyl group is composed of activating substituents, and it is ortho-, para- directing. Substitution ortho or para to the alkyl group gives an intermediate (and a transition state) with the positive charge shared by the tertiary carbon atom. As a result, alkylbenzene undergoes electrophilic aromatic substitution faster than benzene, and the products are predominantly ortho- and para- substituted. The mechanism of linear

alkylbenzene, which is illustrated below, is a two-step process involving electrophilic attack of the nitronium ion on the linear alkylbenzene molecule to form the intermediate mesomeric ion (1), followed by removal of a proton by the hydrogen sulfate ion, which is the most basic species in the reaction mixture.
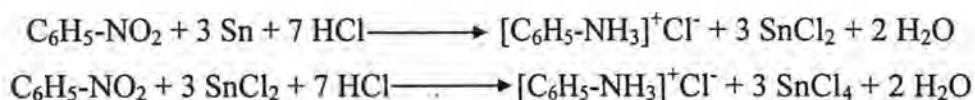
o-attack:
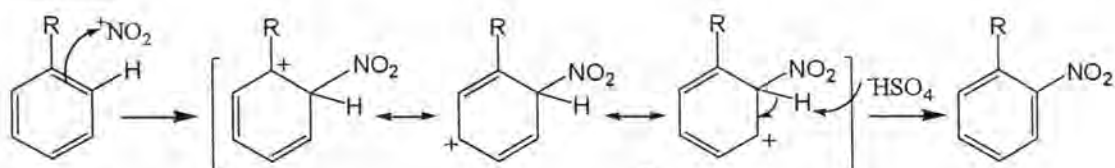
p-attack:
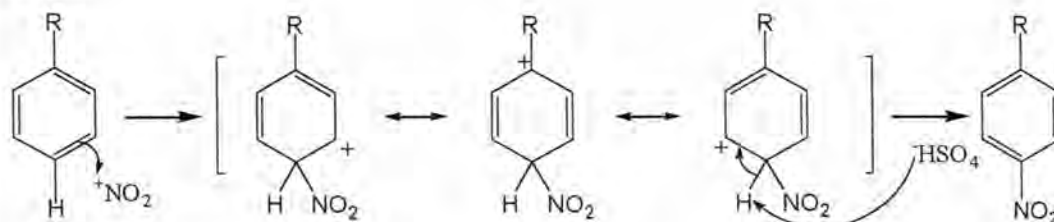
2.6 Reduction reaction [12, 15, 16, 17]

Reduction of aromatic nitro compound is the most useful method of preparing primary aromatic compounds, which is the most important synthetic route in aromatic chemistry. Since the primary aromatic amines are converted into diazonium salts, which can be replaced by a large number of other groups. In addition, diazonium salts can be used to prepare the azo dyes, which are the important class of compounds.
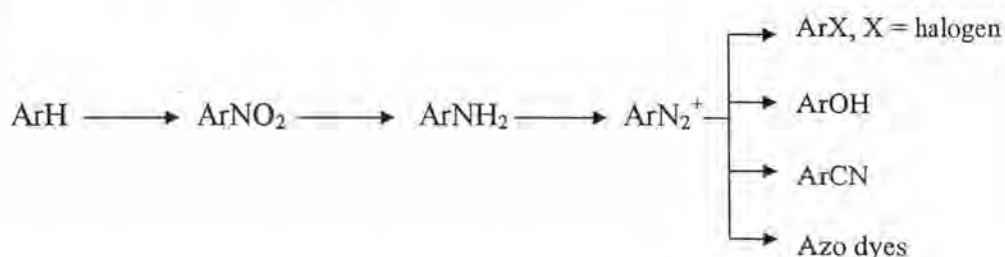

Aromatic nitro compounds can be reduced to primary aromatic amine by catalytic methods and by means of chemical reducing agents, such as tin and hydrochloric acid, stannous chloride and hydrochloric, iron or zinc and acetic acid, sodium sulfide, and others. The reducing agent and the solvent medium can be varied to suit the properties

of the particular nitro compound and aromatic amine. Chemical reduction in the laboratory is most often carried out by adding hydrochloric acid to a mixture of the nitro compound and a meal, usually granulated tin. If the full reducing power of tin and hydrochloric acid were utilized (conversion to stannic chloride), only one and one-half gram-atoms of tin would be required to furnish the six equivalents of hydrogen needed to reduce one mole of nitro compound to aromatic amine.

$$C_6H_5\text{-}NO_2 + 3\ Sn + 7\ HCl \longrightarrow [C_6H_5\text{-}NH_3]^+Cl^- + 3\ SnCl_2 + 2\ H_2O$$
$$C_6H_5\text{-}NO_2 + 3\ SnCl_2 + 7\ HCl \longrightarrow [C_6H_5\text{-}NH_3]^+Cl^- + 3\ SnCl_4 + 2\ H_2O$$

In the reaction mixture the amine is converted to a chlorostannite or chlorostannate salt, $(R\text{-}NH_3)_2SnCl_4$ or $(R\text{-}NH_3)_2SnCl_6$. The free amine is liberated by the addition of sodium hydroxide, and is steam - distilled from the reaction mixture.

$$(C_6H_5\text{-}NH_3)_2SnCl_6 + 8\ NaOH \longrightarrow 2\ C_6H_5\text{-}NH_2 + Na_2SnO_3 + 6\ NaCl + 5H_2O$$
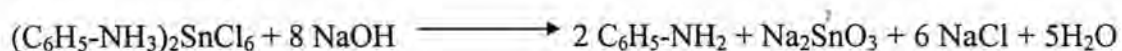
The crude amine is generally contaminated with some unreduced nitro compound. Taking advantage of the basic properties of amine can separate it; the amine is soluble in aqueous mineral acid, and the nitro compound is not.

2.8 Literature reviews

Markers that have been proposed include furfural, quinizarin, diphenylamine, radioactive materials and azo dyes. Azo dyes gain more considerable importance as a marker than others because they can be detected by simple extraction with acid or basic reagent. Furthermore, azo dyes can be detected when they are marked in fuel at a lower concentration than the previous markers. Therefore in recent years, there have been reports on various synthesized azo dyes to be markers, which are listed as follow.

In 1992, Friswell, M.R. et al. synthesized liquid petroleum markers having the following formula [18]:
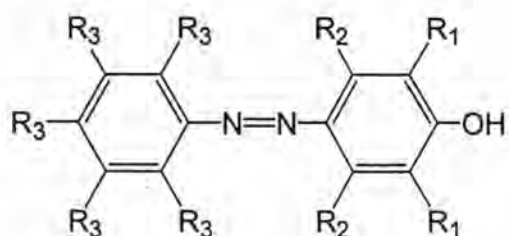
where R_1 and R_2 were each selected from hydrogen and C_1-C_7 alkyl, provided that at least one R_1 was a C_3-C_7 alkyl; R_3 were selected from hydrogen, nitro, halogen, cyano, and methyl, provided that at least one R_3 was selected from nitro, chloro, halogen, and cyano group. These marker compounds were synthesized by azo coupling of appropriate substituted aniline to a 2,6-di-*sec*-butyl phenol. The markers could be detected by extraction with reagent comprising water, water-soluble amine, and a water-miscible cosolvent. This reagent caused the markers to react and develop a clearly defined color that could be used for identifying the petroleum products.

The following year, Hallissy, M.J. synthesized liquid petroleum markers having the formula [19]:
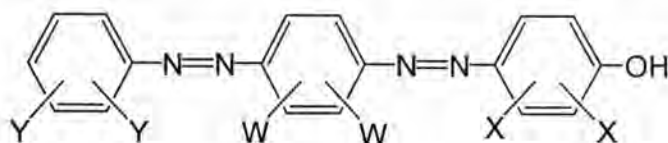

where W_s were selected from O-(C_1-C_3 alkyl) and hydrogen, provided that at least one W was O-(C_1-C_3 alkyl). X_s and Y_s were selected from hydrogen, alkyl, substituted alkyl, alkenyl, substituted alkenyl, aryl, substituted aryl, fused aryl, substituted fused aryl, halogen, nitro, cyano, and alkoxy group. These markers were conveniently synthesized by azo coupling of appropriate substituted aniline to a phenol, such as 2,6-di-*sec*-butylphenol. Although these compounds were generally pale red, they were not readily observable by the naked eye when they were added into petroleum products at the level of 0.25 to 100 ppm. The markers could be detected by extraction with alkali aqueous solution, e.g., 1-3% sodium hydroxide solution. And the quantity amount of marker was determined in aqueous phase by colorimetric equipment.

In 1996, Brenzinger, R.D. et al. invented a method for detecting marked mineral oils using an azo dye of the formula [20]:
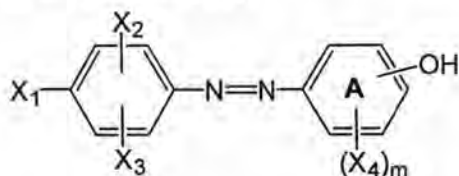

where the ring A might be benzofused; m was from 1 to 4; X_1 was hydrogen, C_1-C_4 alkyl, cyano or nitro; X_2 was hydrogen, C_1-C_4 alkyl, cyano, nitro, C_1-C_4 alkoxy or C_1-C_{16} alkoxycarbonyl; X_3 was hydrogen, C_1-C_4 alkyl, cyano, or C_1-C_{16} alkoxycarbonyl ; X_4 was hydrogen, hydroxyl, substituted or unsubstituted C_1-C_8 alkyl, C_1-C_4 alkoxy, amino, C_1-C_4 dialkylamine, or substituted or unsubstituted C_1-C_{16} monoalkylamino. These markers could be detected by treating the marked mineral oils with an extractant comprising water, water-miscible organic solvent and a base such as an alkali or alkaline earth metal hydroxide, an alkali metal carbonate or a quaternary ammonium hydroxide. This reagent was transferred the azo dye from the mineral oil into the aqueous phase, which took on distinctly visible color.

In the same year, Friswell, M.R. et al. synthesized petroleum fuels markers having the general formula [3]:
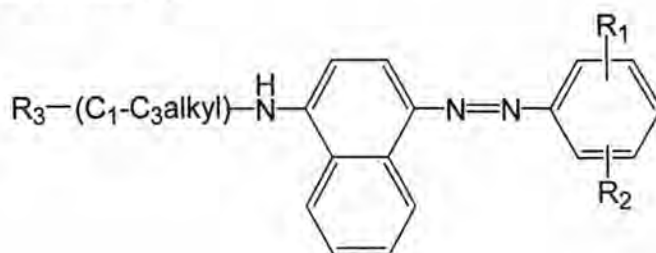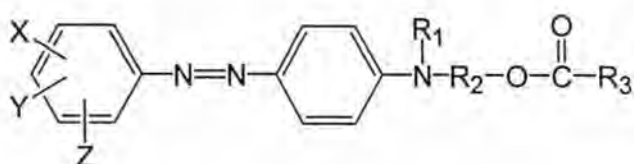

where R_1 and R_2 were selected from hydrogen, methyl, ethyl, methoxy, halogen, cyano, and nitro group; R_3 was selected from methyl, methoxy, ethoxy, morpholino group. These markers were synthesized by azo coupling of substituted aniline to an alpha-naphthylamine. They were generally colorless or had a pale yellow color in petroleum products. These tagged petroleum products were extracted with acidic aqueous solution, e.g., a 10% hydrochloric, formic acid or phosphoric acid solution, which gave various colors in the aqueous phase depending on the substituents in the molecule.

A year later, Brenzinger, R.D. et al. synthesized aniline derivatives, which were used for marking mineral oil. These aniline derivatives had the formula [21]:
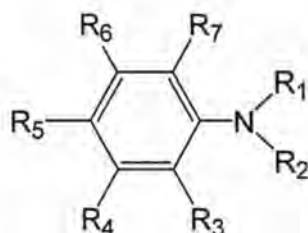

where R_1 and R_2 were each hydrogen, unsubstituted or substituted alkyl, alkenyl or phenyl group; R_3 and R_4 were each hydrogen, unsubstituted or substituted alkyl, alkenyl, cyano, nitro, acyl, or acylamino group; R_4 was hydrogen, unsubstituted or substituted alkyl, alkenyl, hydroxy, amino, carboxyl, or sulfamoyl group; R_5 and R_6 were each hydrogen, unsubstituted or substituted alkyl, alkenyl, phenyl, nitro, acylamino, or carboxyl group. They could be detected by treatment with an aqueous solution of the diazonium salt, which was derived from an amine of the aminoanthraquinone, aminonaphthalene, aminothiophene, or aminobenzoisothiazole series. Then an azo dye was formed, which will give the different color in the aqueous phase.

In 1998, Friswell, M.R. synthesized the marker dyes having the general formula [22]:

where R_1 was C_1-C_3 alkyl; R_2 was C_1-C_3 alkylene; R_3 was C_1-C_2 alkyl, preferably C_1-alkyl; X and Y were selected from hydrogen, methyl, ethyl, methoxy, halogen, and nitro; Z was hydrogen or
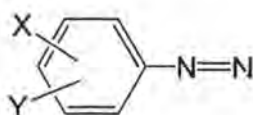
wherein X and Y were as defined above.

These compounds known as "solid dispersed dye" were synthesized in a two-phase system, including an acidic aqueous phase and a solvent phase. The tagged petroleum fuels at levels from about 0.25 to about 100 ppm were extracted with acidic aqueous solution, where the marker underwent a chromophoric reaction, developing a strong color in the aqueous extraction solution.

In the same year, Zeidler, G. et al. synthesized azo dyes having the formula [23]:
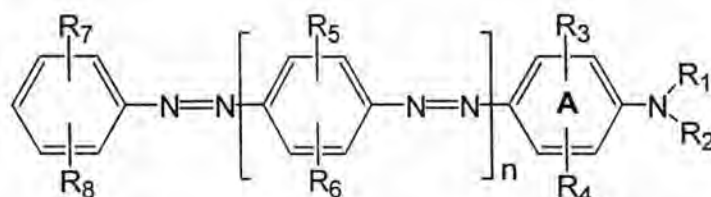
where the ring A might be benzofused; n was 0 or 1; R_1 was hydrogen or C_1-C_{15} alkyl, which might be interrupted by from 1 to 4 ether oxygen atoms; R_2 was C_1-C_{15} alkyl, which might be interrupted by from 1 to 4 ether oxygen atoms, or a radical of the formula L-NX_1X_2, where L was C_2-C_8 alkylene and X_1 and X_2 independently of one another were each C_1-C_6 alkyl, or together with the hydrogen atom linking them, form a 5-membered or 6-membered saturated heterocyclic radical. This radical may furthermore contain an oxygen atom in the ring; R_3, R_4, R_5, R_6, and R_7 independently of one another were each hydrogen, C_1-C_{15} alkyl, or C_1-C_{15} alkoxy; R_8 was hydrogen, C_1-C_{15} alkyl, C_1-C_{15} alkoxy, cyano, nitro, or a radical of the formula $COOX_3$, where X_3 was hydrogen, C_1-C_{15} alkyl, which might be interrupted from 1 to 4 ether oxygen atoms, or was a radical of the formula L-NX_1X_2, where L, X_1 and X_2 each had the above-mentioned meanings.

These azo dyes could be used as pH-dependent markers in particular mineral oils such as gasoline, kerosine or diesel. They were detected by the action of aqueous alcoholic solutions of a protic acid, in the presence or absence of a zinc halide, aluminum halide or tin halide. The consequence was a color reaction, i.e. a color change, which was accompanied by deepening of color.

In 1999, Changmongkol synthesized marker dyes by coupling reactions of alkylsalicylate compounds and the esterified cashew nut shell liquid with diazonium salt of methyl aniline derivatives [24]. The formula of these marker dyes are shown below.


where $n = 0, 2, 4, 6$
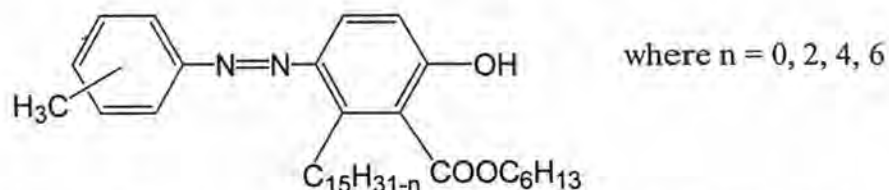
These marker dyes were added into diesel oil at low concentration, which could be detected by extracting the marked diesel oil with appropriate solvent extraction systems. The extracted phase of these markers were yellow.

At the same time, Chongpiyawarang synthesized marker dyes in homologous series of chloronitroaniline having the formula [25]:


where $n = 0, 2, 4, 6$
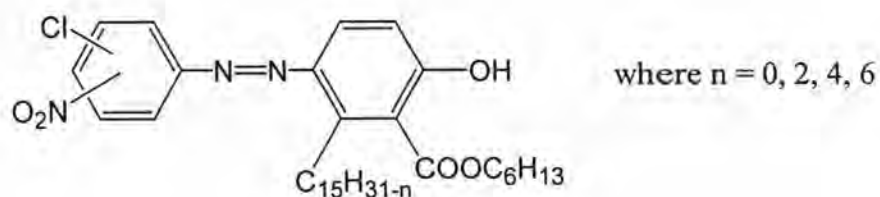
These marker dyes were synthesized by the coupling reaction of alkylsalicylate compounds and the esterified cashew nut shell liquid with diazonium salt of chloronitroanilines. Each of the marker dyes was added into diesel oil at low concentrations and found that they did not alter the physical and chemical properties of the marked diesel oil. The method for detecting was achieved by treating the appropriate solvent extraction system comprising co-solvent systems and base. The quantitative determinations were required to measure the concentrations of marker dyes in diesel in case of dilution, adulteration, and storage stability.

Keosaeng, synthesized amino azo dyes as marker dyes for fuel oils having the formula [26]:
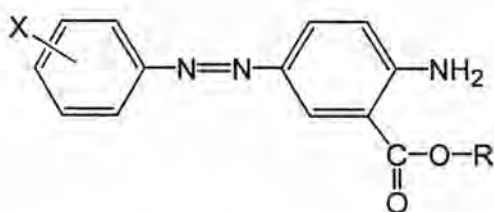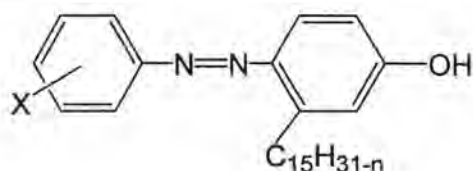
where X was selected from hydrogen, nitro, chloro, or methyl group and R was selected from ethyl or hexyl group. These marker dyes were prepared by a coupling reaction of diazonium salt of aniline derivatives, with amino benzoates. They could be detected at low levels (about of 1 to 6 ppm) by extraction with alkali medium solution, which developed the clearly defined color in the extracted phase.

Silapakampeerapab synthesized marker dyes having the formula [4]:
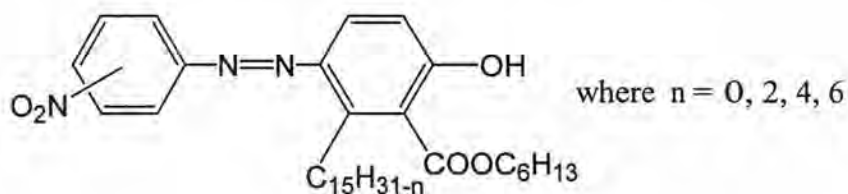
where n = 0, 2, 4, 6

These marker dyes were synthesized by a coupling reaction between extracted esterified cashew nut shell and nitro anilines. They were used as marker dyes in gasoline and high-speed diesel at treat rate of 25 and 15 ppm, respectively, which could be detected by extraction of marked fuel oils with 2% potassium hydroxide in ethylene glycol, and then gave clearly defined color in an extracted phase.

Moreover, Suwanprasop synthesized marker dyes for petroleum products having the formula [6]:

where X was selected from hydrogen, nitro, chloro, methyl, or methoxy group, n was 0, 2, 4 and 6. These marker dyes were prepared by a coupling reaction of cardanol, which was obtained from partial purification of decarboxylated cashew nut shell

liquid, with diazonium salt of aniline derivatives. They were added into gasoline and high-speed diesel at levels of 2 to 5 ppm. Their presence could be detected by extraction into an appropriate alkali aqueous solution, which provided visually intense colors.

Finally, Thowongs synthesized marker dyes for petroleum fuel having the formula [5]:
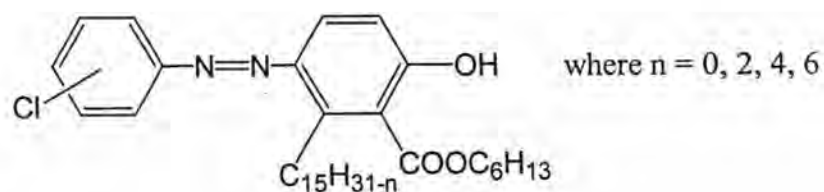
$$\text{Cl}-\underset{\underset{C_{15}H_{31-n}}{}}{\bigcirc}-N=N-\underset{\underset{COOC_6H_{13}}{}}{\bigcirc}-OH \qquad \text{where } n = 0, 2, 4, 6$$

These marker dyes were synthesized by a coupling reaction between extracted esterified cashew nut shell and chloro anilines. The esterified cashew nut shell extracted was obtained from the esterification reaction between extracted cashew nut shell and 1-hexanol. These marker dyes were used at treat rate of 30 ppm in gasoline and high-speed diesel. They could be detected by extracting with 10% potassium hydroxide in methanol, which gave a yellow color in an extracted phase.