

## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 Dye and Light absorption [3, 6, 7]

##### 2.1.1 Dye

A dye is defined as an organic compound that is used to impart color from other substances in an aqueous medium. The property of a dye is to retain its color on prolonged exposure to light or to resist removal under conditions to which the substances normally are exposed. Dyes are defined according to either the type of chemical compound that they represent or the method of application for which they are principally useful. A very brief definition of each of the more important types is, therefore, in order as shown below.

##### 2.1.1.1 Application of dyes

-Basic and Acid Dyes These dyes contain either basic or acidic groups; and for dyeing from an aqueous solution, they are rendered soluble by salt formation.

-Direct Dyes These dyes, usually acid dyes, have affinity for cotton from a neutral solution, generally in the presence of an electrolyte, such as sodium chloride or sodium sulfate.

-Azoic Dyes or Developed Dyes These dyes are capable of undergoing reactions on the fiber to produce less soluble dyes having improved fastness to washing.

-Vat Dyes Vat dyes are compounds capable of reduction to a soluble "leuco" or highly colored form that has affinity for the fiber and is readily reoxidized on the fiber to the organic dye. These dyes class offer the best all-around fastness, especially to light and washing.

-Sulfur Dyes These dyes differ from vat dyes in that they always contain sulfur and the reduction requires sodium sulfide, whereas sodium hydrosulfite is used for vat dyes.

-Mordant Dyes These dyes are capable of combining with various metals to form complexes of different types.

-Disperse Dyes Dyeing of cellulose acetate, polyester, or other synthetic fibers can be brought about by colloidal aqueous dispersions of azo or anthraquinone dyes that have low molecular weight, lack sulfonic acid groups, and are soluble in the organic polymer.

-Fiber-Reactive Dyes The simple acidic and basic dyes are substantial to wool and silk and yield brilliantly colored fibers.

-Oil-and Spirit-Soluble Dyes These dyes are used to dye gasoline, plastic, fats, oils and waxes, spirit printing inks, and stains.

-Fluorescent Brightening or Optical Whitening Agents These dyes are known as direct whites, optical bleaches, or Blankophores. Colorless compounds that have an affinity for fibers and have a blue fluorescence when exposed to near ultraviolet light are used extensively as whitening agents.

-Food Drug, and Cosmetic Color Certain dyes are toxic and some even promote the growth of tumors. Hence most nations permit the coloring of foods, drugs, and cosmetics only with these dyes which are considered to be harmless.

#### 2.1.1.2 Chemical Classes of dyes

-Azo Dyes These dyes are the largest single group of dyes, making up over half of the total number of synthetic colors of known structure. Most azo dyes are sodium salts of sulfonic acids. Those of high molecular weight, containing two, three, and four azo groups (diazo, triazo, and tetrakisazo dyes) are substantial for cotton. Azo dyes are prepared by coupling a diazotized aromatic amine with a phenol or an aromatic amine. In the benzene series, coupling takes place *para* to the hydroxyl or amino group, or *ortho* if the *para* position is occupied. If all *ortho* and *para* positions are occupied, no coupling takes place. The azo grouping is responsible for the color of these compounds, and such a group is known as a chromophore. The shade of the color is affected by substituting in the benzene rings, and the substance is able to function as a dye and become attached to cloths only when salt forming groups are in the ring (auxochrome group). Most of the azo dyes are some shade of yellow or red, although shades approaching blue may be secured with certain structures.

-Stilbene Dyes These dyes are derivatives of 4,4'-diamino-2,2'-stilbenedisulfonic acid, which are made by the reduction of the dinitroso compound. They account for over 80 per cent of the fluorescent brightening agents.

-Triphenylmethane dyes These dyes are basic dyes for wool or silk, or for cotton mordant with tannic acid. They are not fast to light or washing, except when applied to acrylic fibers.

-Indigoid Dyes The oldest known recorded use of an organic dye is that of the vat dye, indigo. Egyptian mummy cloths, estimated to be over four thousand years old, were dyed with it.

### 2.1.2 Light absorption [6, 13, 18]

The human eyes are sensitive to a very small portion of the electromagnetic spectrum. The portion of this spectrum derives from wavelengths of about 400 nanometres (nm) to 700 nanometres (nm). Visible colors are due to differences in the wavelengths of light in this region that reaches the eyes. One of two processes is involved when we observe color. An object may emit or absorb light of a certain wavelength and reflect light of the other wavelengths back to the human eyes. The most important source of color in organic compounds is the absorption of light without subsequent emission. The absorbed energy is dissipated into molecular motions. Many organic compounds absorb certain wavelengths of white light and reflect the rest. However, the sensitivity of the human eyes depend on intensity of the radiation source, the conditions under which observation is made, and to some extent the individual making observation.

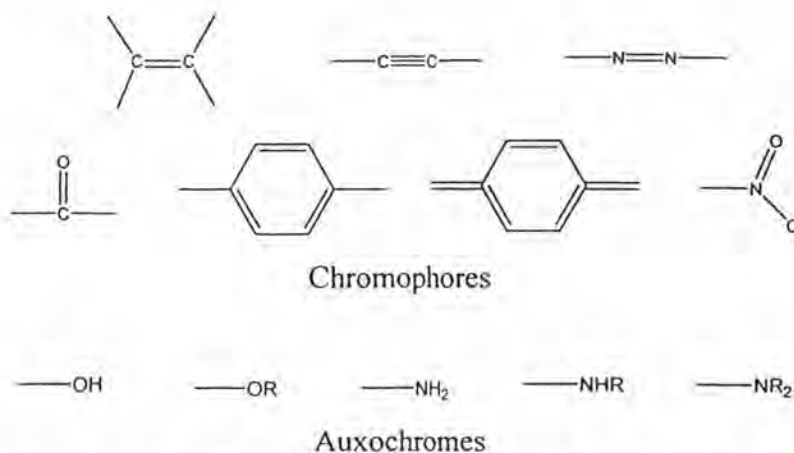
**Table 2-1: Relation between light absorption and visual color**

Wavelengths Absorbed (nm)	Color Absorbed	Visual Color
400-435	Violet	Yellowish-green
435-480	Blue	Yellow
480-490	Greenish-blue	Orange

**Table 2-1: Relation between light absorption and visual color (continue)**

Wavelengths Absorbed (nm)	Color Absorbed	Visual Color
490-500	Bluish-green	Red
500-560	Green	Purple
560-580	Yellowish-green	Violet
580-595	Yellow	Blue
595-605	Orange	Greenish-blue
605-700	Red	Bluish-green

For an organic compound to appear colored, it must absorb light in the visible region of the electromagnetic spectrum. In order to do that, it must have a long conjugated pi system. The types of groups containing easily excited pi systems that can absorb visible light are called chromophores (from the Greek *chroma* color, *phoros* from phere in to bear). At least one chromophore must be present in a molecule for the compound to be colored. Others groups in a molecule may augment the absorption of light. These groups are called auxochrome (Greek *auxanein* to increase). Auxochromes do not cause color in a structure, but deepen the color imparted by the chromophores.



It is shown that the more the conjugation is extended, the number of molecular orbital is greater and the closer their energy levels are spaced. Hence less

energy is required for electronic transitions, and absorption is shifted to longer wavelengths. The interaction of auxochromes with the conjugated system not only extends the conjugation but also leads to large dipole moments and large transition dipole moments with resulting high-intensity absorption. Acylation of an amino or a hydroxyl group merely decreases the availability of an unshared pair of electrons for interaction with the conjugated system.

Measurement of the absorption of ultraviolet and visible radiation by species in solution provides one of the most widely used methods of quantitative analysis available in laboratory. The generation of a suitable absorbing species in solution in amounts is quantitatively related to the amount of analyte to be determined. The Beer-Lambert law tells that the absorbance depends on the total amount of the absorbing species in the light path through the cell, and this means that the absorption is affected by both concentration ( $c$ ) and path length ( $l$ ).

This law applies strictly only to monochromatic light (that is light of a single wavelength) and depends on the absorbing system being homogeneous. The Beer-Lambert Law can be written in the simple form:

$$A = a c l$$

Where  $A$  is the absorbance,  $a$  is a proportionality constant known as the absorptivity. Absorptivity is a constant for a particular compound in a particular solvent at a particular wavelength, but it may have different numerical values depending on the units employed.

When the molar concentrations of the compound is known, it is common to calculate the molar absorptivity or molar absorption coefficient ( $\epsilon$ ). This quantity is a measure of the intensity of absorption of radiation of a particular wavelength by the solute. The maximum value of  $\epsilon$  ( $\epsilon_{\max}$ ) is commonly quoted for substances as a useful characteristic of their absorption bands, together with the wavelengths ( $\lambda_{\max}$  values) at which maximum absorption occurs.

Rearranging the Beer's law and substituting  $\epsilon$  for  $a$  obtain

$$\epsilon = A / c l$$



By using value of concentration and path-length in units of  $\text{mol dm}^{-3}$  and  $\text{cm}$ , respectively, we can calculate  $\epsilon$  which will have units of  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  or  $\text{m}^2 \text{mol}^{-1}$ . Note that absorbance is dimensionless and hence has no units.

Finally, there are various phrases used in connection with electronic absorption spectroscopy, and for completeness some of these are explained in the following list:

- Bathochromic shift Displacement of an absorption band towards longer wavelengths.
- Hypsochromic shift Displacement of a band to shorter wavelengths.
- Red shift Synonymous with the term bathochromic shift, implying a movement towards the red end of the spectrum.
- Blue shift Synonymous with hypsochromic shift, i.e. a movement towards the blue end of the spectrum.
- Deepening in color This rather ambiguous phrase is occasionally encountered, and refers to a bathochromic shift specifically in the visible region of the spectrum. It does not imply an increase in the absorption intensity.
- Hyperchromic effect An increase in the intensity of an absorption band.
- Hypochromic effect A decrease in the intensity of an absorption band.
- Solvatochromism The change in position and intensity of absorption band accompanying a change in the polarity of the solvent.
- Halochromism The color change (i.e. displacement of the visible absorption band) of a substance accompanying a change in the pH of the solution.
- Half-band width The width of an absorption band (usually expressed in wavenumber units) at one half the total peak height.

## 2.2 Marker Dyes [24]

A marker is a substance that can be added into petroleum products for subsequent detection. The marker is dissolved in a liquid to be identified. It is rapidly detected by performing a simple physical or chemical test on the marked liquid. The important characteristics of certain desirable markers for petroleum are as follows:

1. They are entirely foreign to the liquids.

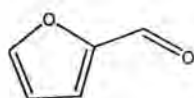
2. They can be supplied as highly concentrated solutions supplied in compatible solvents.
3. They are easily detected by a simple field test.
4. They are not obscured by unstable natural components of the liquids.
5. They can be stable over the anticipated storage life of the tagged liquid (usually three to six months).
6. They have identities that can be confirmed by laboratory methods.

The marker dyes are preferably used in the form of concentrated solution owing to their easiness of use, rapidity of dosage, and high diffusion coefficient. In such manner, they cannot be observed in the petroleum product until appropriately extracted in concentrated form from the petroleum product. An extracted solution must be a petroleum-immiscible solution that should remove substantially all marker dyes from the specimen of the petroleum product being tested.

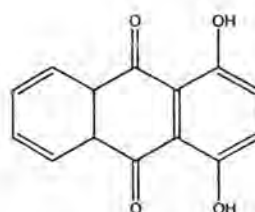
The dyes that may be used in the coloring of such petroleum products such as, gasoline, kerosine, gas oil, must render identifiable of them for a purpose that differ from the ones for which they are taxed, and fulfill various requirements, i.e. among other:

1. They poss a high dyeing power.
2. They have a sufficient solubility in the solvents and fuel.
3. They have a high diffusion index.
4. They contain little or no by-product insoluble in oil.
5. They leave only a minimum deposit of sludge in the engines.
6. They have a proper fastness to light during storage.
7. They are compatible with additives and do not cause difficulties during combustion.
8. They are brittle but not powderous in the solid form.
9. They are sufficiently fluid to be solubilized in organic solvents, if used in the form of a concentrated solution.

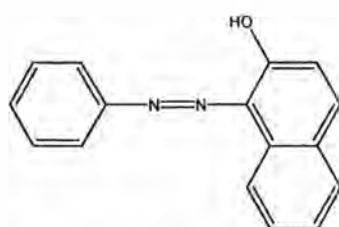
However, all these characteristics are not sufficient for the choice of a suitable dye since the dye is difficult to extract from the system in which it is dissolved. Instances of marker dyes used to mark fuel oil are shown below.



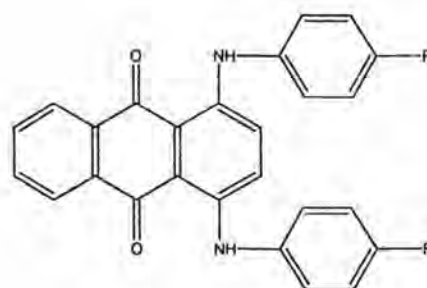
Furfural



Quinizarin



Solvent Yellow 14

Where R = H, CH<sub>3</sub>

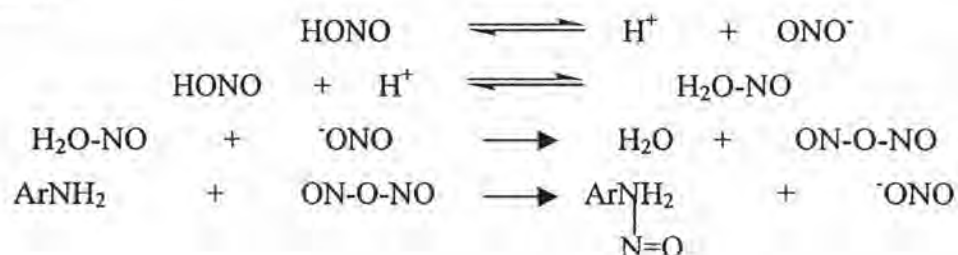
Solvent Blue 76, Solvent Green 3

## 2.3 Preparation of Azo Dyes [12]

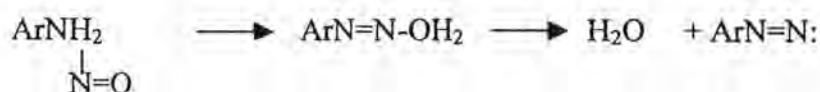
### 2.3.1 Diazotization

Generally, aromatic diazonium compounds are not isolated but are prepared and used in aqueous solution. The reaction of the amine salt with nitrous acid is known as diazotization and must be carried out in strongly acid solutions to prevent the diazonium salt from coupling with unreacted amine. The nitrous acid is generated by the addition of sodium nitrite to the suspension of amine salt in excess mineral acid. Most diazonium salts are unstable at room temperature. Hence the reaction is carried out at 0°C and the solution is used immediately.

Resonance symbols show the delocalization of the positive charge in the benzene diazonium ion. The diazotization reaction proceeds according to the equation:



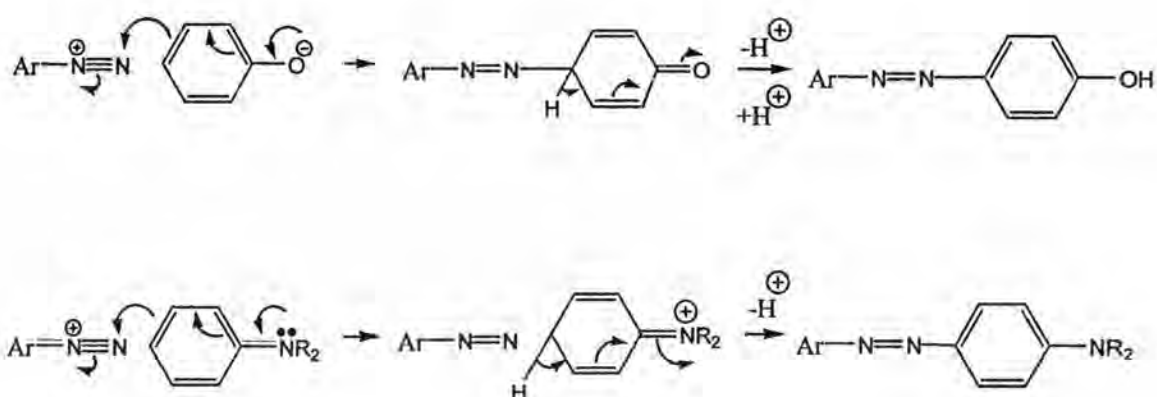




### 2.3.2 Coupling Reaction [8]

The coupling reaction is an electrophilic substitution involving the diazonium ion, which reacts at the position of greatest electron availability, i.e. the position *ortho* or *para* to the electron releasing phenoxy and amino groups. Coupling takes place only in weakly acid, neutral, or alkaline solutions. In strongly acid solutions the hydroxy group is undissociated, and the amino group is present as its salt. Only the free amino group and the oxide ion are sufficiently activating to permit coupling.

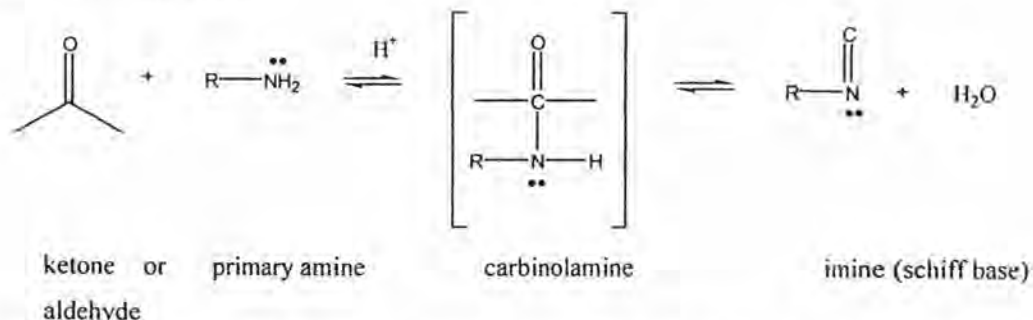
In the coupling reaction, the diazonium salt is known as the *primary component*, and the compound with which it couples is called the *secondary component*. Coupling takes place in the unhindered *para* position of the secondary component. If the *para* position is occupied, coupling takes place in the *ortho* position. If the *para* position and both *ortho* positions are blocked, coupling usually does not take place, although occasionally the group in the *para* position is displaced. Diazo coupling products are brightly colored and some are used as dyes.



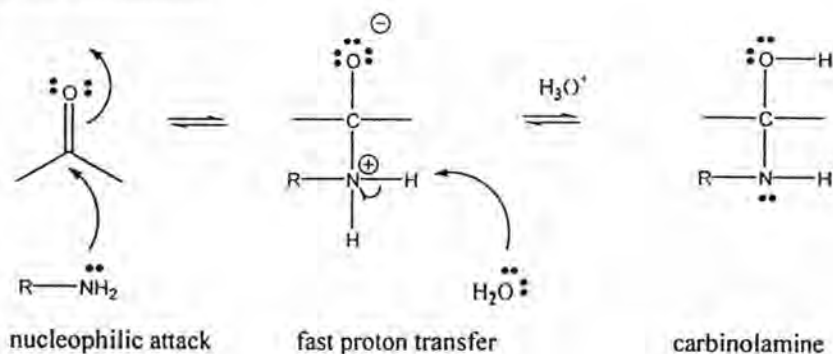
### 2.4 Formation of imine [25]

Under the proper conditions, either ammonia or a primary amine reacts with ketone or an aldehyde to form an imine. Imines are nitrogen analogues of ketones and aldehydes, with a carbon-nitrogen double bond in place of the carbonyl group. Like amines, imines are basic; a substituted imine is also called a Schiff base. Imine

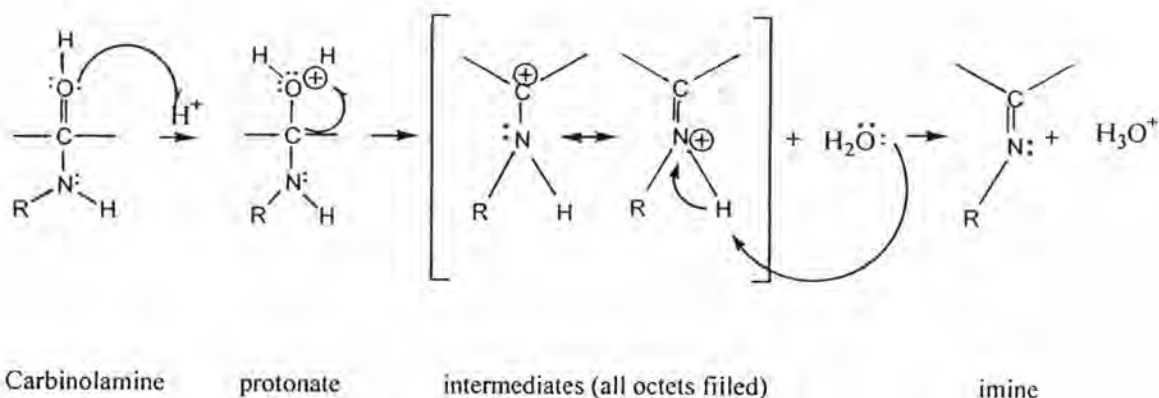
formation is an example of a large class of reactions called condensations, reactions in which two (or more) organic compounds are joined, with the elimination of water or another small molecule.



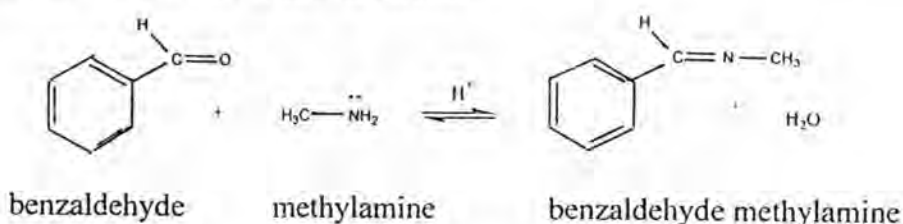
The mechanism of imine formation begins with a basic nucleophilic addition of the amine to the carbonyl group. Attack by the amine followed by protonation of the oxygen atom (and deprotonation of the nitrogen atom) gives an unstable intermediate called a carbinolamine.



A carbinolamine reacts to form an imine by the loss of water and formation of a double bond: a dehydration. This dehydration follows the same mechanism as the acid-catalyzed dehydration of an alcohol. Protonation of the hydroxyl group converts it to a good leaving group, and it leaves as water. The resulting cation is stabilized by a resonance structure with all octets filled and the positive charge on nitrogen. Loss of a proton gives the imine.



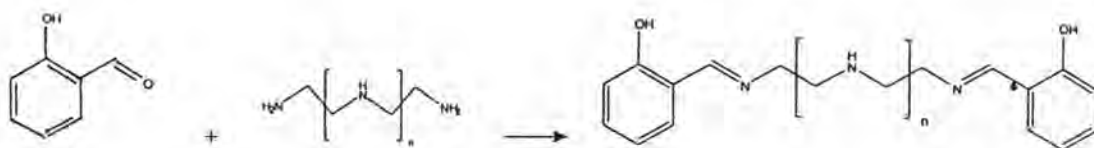
The C=O group of the ketone or aldehyde is replaced by the C=N-R group of the imine. The instance reaction is shown below.



## 2.5 Reactions in this research

### 2.5.1 Preparation of imines

Imines in this research are synthesized from reaction of salicylaldehyde and primary amines, e.g. ethylenediamine, diethylenetriamine, and triethylenetetramine in methanol solution, which is cooled in an ice bath. The reactions are schemed below.

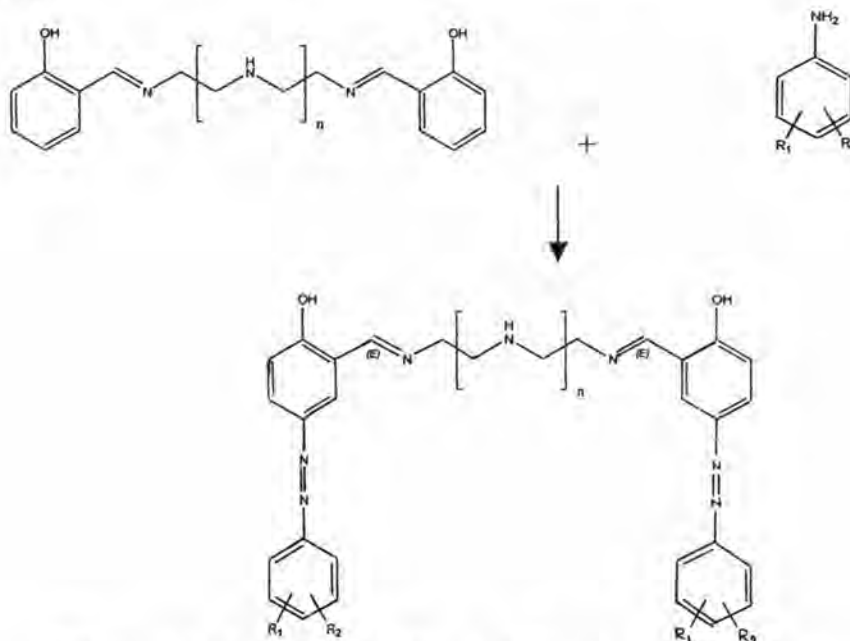


Where n is 0, 1, 2.

### 2.5.2 Coupling reaction of imines and aniline derivatives

Marker dyes in this research are synthesized by coupling reaction of diazonium ion with synthesized imines in an alkaline solution. Since many diazonium

ions decompose rapidly in solution, it is necessary to use freshly prepared diazonium ions and synthesize them under deep cold conditions. The reactions are schemed as shown below.

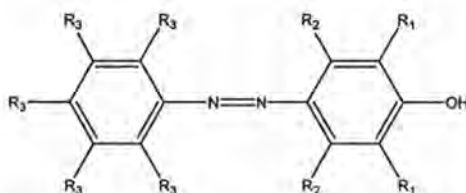


Where  $n$  is 0, 1, 2, and  $R_1$ , and  $R_2$  are substituent group such as hydrogen, nitro group, chloro group, etc.

## 2.6 Literature Review

There have been many inventions of markers for fuel oil for a long time. Both marker dyes and silent markers were invented.

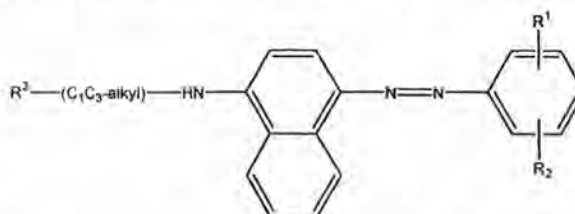
Friswell, M.R. and Orelup, R.B. [10] invented the markers of the general class of chemicals as phenylazophenols having the formula,



wherein the  $R_1$ 's and the  $R_2$ 's were the same or different and each was selected from  $-H$  and  $C_1$ - $C_7$  alkyls, provided that at least one, and preferably both,  $R_1$ 's were a  $C_3$ - $C_7$  alkyl; and provided that the  $R_3$ 's were the same or different and are selected from  $-H$ ,  $-NO_2$ ,  $-Cl$ ,  $-Br$ ,  $-F$ ,  $-CN$ , and  $-Me$ ; and provided that at least one  $R_3$  was

selected from  $-\text{NO}_2$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{F}$  and  $-\text{CN}$ . The markers might be detected in the petroleum products by extraction with a reagent comprising water and a water-soluble amine, and preferably a water-miscible co-solvent.

Later Friswell, et al. [9] also invented the silent markers for tagging petroleum fuels and detection procedure of such markers by extraction with an acidic aqueous solution such as 10% HCl. These silent markers have the formula shown below:



where  $\text{R}^1$  and  $\text{R}^2$  were selected from H, methyl, ethyl, methoxyethoxy, and morpholino group.

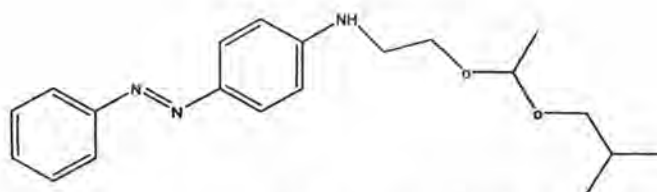
Hallisy, M.J. [14] invented the silent markers having the formula as follows:



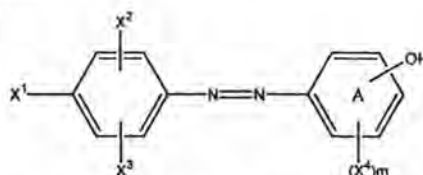
where the Ws were selected from O-( $\text{C}_1$ - $\text{C}_3$  alkyl) and hydrogen, provided that at least one W is O-( $\text{C}_1$ - $\text{C}_3$  alkyl), the Xs and Ys were the same or different and were selected from hydrogen, alkyl, substituted alkyl, alkenyl, substituted alkenyl, aryl, substituted aryl, fused aryl, substituted fused aryl, halogen, nitro, cyano, and alkoxy. Hallisy also studied the detection procedure of tagged petroleum products which can be detected by extraction with an alkaline aqueous solution such as 50/50 by volume mixture of water and methanol containing 2% by weight of NaOH.

Henricsson, S. and Westerholm, R. [15] studied a liquid chromatographic method for analyzing the color marker, Solvent Yellow 124, in diesel fuel. The method was robust and could easily be adapted by a routine laboratory; the throughput of samples could be as high as 180 samples per day, with a minimum of sample pretreatment. The coefficient of variation was 5.2% for a diesel fuel containing 5 mg/l of the colored marker dye. An application of this method for analyzing uncombusted residues from diesel engines and oil-fired boilers was also described.



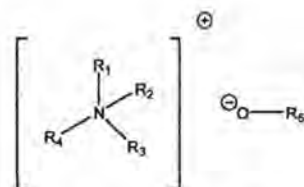


Rainer et al. [18] studied the method for detecting marked mineral oils by treating with an extractant comprising water, a solvent and a base, and the invented azo marker dyes having the formula:



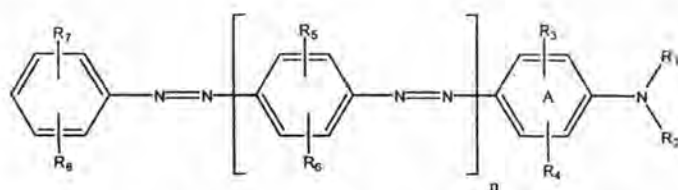
where ring A might be benzofused, m was from 1 to 4,  $X^1$  is hydrogen,  $C_1$ - $C_4$ -alkyl, cyano or nitro,  $X^2$  was hydrogen,  $C_1$ - $C_4$ -alkyl, cyano, nitro,  $C_1$ - $C_4$ -alkoxy or  $C_1$ - $C_{16}$ -alkoxycarbonyl,  $X^3$  was hydrogen,  $C_1$ - $C_4$ -alkyl, cyano or  $C_1$ - $C_{16}$ -alkoxycarbonyl, and  $X^4$  was hydrogen, hydroxyl, substituted or  $C_1$ - $C_8$  alkyl,  $C_1$ - $C_4$ -alkoxy amino,  $C_1$ - $C_4$ -dialkylamino or substituted or unsubstituted  $C_1$ - $C_{16}$ -monoalkylamino. A solvent and a base extractant were alkali or alkaline earth metal hydroxide, an alkali metal carbonate or a quarternary ammonium hydroxide. The use of novel azo dyes as markers for mineral oils were also described.

Smith, M.J. [21] studied the compositions for and methods of detecting or developing base reactable fuel markers. Developing agents of its present invention contain quarternary or tetra alkyl ammonium hydroxides or alkoxide of the following formula:



Where  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  were the same or different alkyl or benzyl groups and  $R_5$  was hydrogen or an alkyl group.

Zeidler et al. [26] described the use of azo dyes of the formula

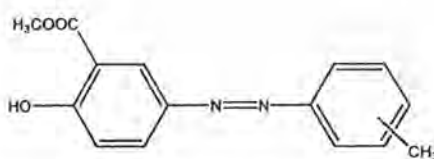


where the ring A might be benzofused,  $n$  was 0 or 1,  $R^1$  was H or  $C_1$ - $C_{15}$ -alkyl which might be interrupted by from 1 to 4 ether oxygen atoms.  $R^2$  was  $C_1$ - $C_{15}$ -alkyl which might be interrupted by from 1 to 4 ether oxygen atoms, or a radical of the formula  $L-NX^1X^2$ , 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 nitrogen atom linking them, form a 5-membered or 6-membered saturated heterocyclic radical which might 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 H,  $C_1$ - $C_{15}$ -alkyl or  $C_1$ - $C_{15}$ -alkoxy. And  $R^8$  was H,  $C_1$ - $C_{15}$ -alkyl,  $C_1$ - $C_{15}$ -alkoxy, cyano, nitro or a radical of the formula  $COOX^3$ , where  $X^3$  was H,  $C_1$ - $C_{15}$ -alkyl which might be interrupted by from 1 to 4 ether oxygen atoms, or was a radical of the formula  $L-N-X^1X^2$ , where  $L$ ,  $X^1$  and  $X^2$  each had the above-mentioned meanings. As pH-dependent markers for hydrocarbons, hydrocarbons containing the above-mentioned azo dyes, and a process for detecting these azo dyes in hydrocarbon and novel azo dyes were also described.

Zoumalan, S. [27] studied a method for analyzing the concentration of a trace, e.g. nitrogen-bearing marker dye (Marker MP Dye), in a hydrocarbon liquid, e.g. gasoline. In the present method, a sample of the marked hydrocarbon liquid was prepared by adding a known volume of a nitrogen-bearing to the internal standard. It was then heated, preferably in a gas chromatograph, to measure the dye and the internal standard. These measurements provided a ratio which is matched or compared to a predetermined reference ratio which, in turn, is representative of a known concentration of the dye in the sampled hydrocarbon.

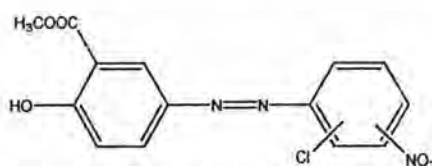
In Thailand, there are many researches related to marker dyes including:

Changmonkol, S. [4] synthesized marker dyes by coupling reactions between alkylsalicylate compounds and the esterified cashew nut shell liquid with methylaniline derivatives. These marker dyes had the following formula:



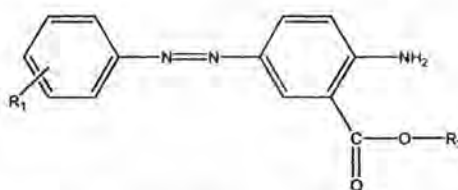
Each of the marker dyes was added into diesel oil at low concentrations meaning that they did not have any effects on the physical and chemical properties of the marked diesel oil. The method for detecting was extraction with the appropriate solvent extraction systems. The quantitative determinations were studied by measuring the marker dyes' concentrations in diesel oil in case of dilution and storage stability.

Chongpiyawarang, S. [5] synthesized marker dyes in homologous series of chloroanilines by coupling reactions between alkylsalicylate compounds and the esterified cashew nut shell liquid with four types of chloroanilines. These marker dyes had the following formula:

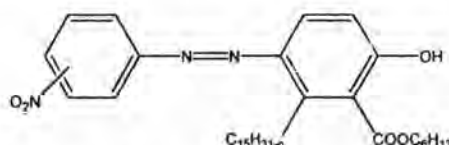


Each of the marker dyes was added into diesel oil at a low concentration and it was found that they did not alter the physical and chemical properties of the marked diesel oil. The method for detecting was achieved by treating the appropriate solvent extraction systems comprising co-solvent systems and base. The quantitative determinations were required to measure the marker dyes' concentrations in diesel oil in case of dilution, adulteration and storage stability.

Keowsaeng, K. [16] invented amino azo dyes as marker dyes for fuel oil, which were prepared from coupling reaction of diazonium salts of nitroanilines, chloroanilines, toluidines and 2-chloro-4-nitroaniline and aminobenzoates such as ethyl-2-amino benzoate and hexyl-3-aminobenzoate. Amino azo dyes having substituent groups as nitro group in ortho and para position, except hexyl-3-aminobenzoate, 5-[(2-nitrophenyl) azo] were suitable to use as marker dyes in fuel oil. These markers were detected by extraction with alkaline medium solution. The amount of added marker might be detected at low level about 1 to 6 ppm might be detected. The structure of these synthetic marker dyes was shown below.

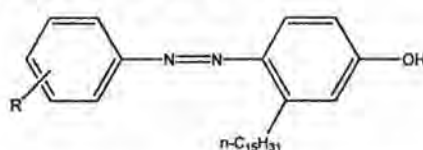


Silpakampeerapab, S. [20] invented the synthetic petroleum fuel markers having the formula:



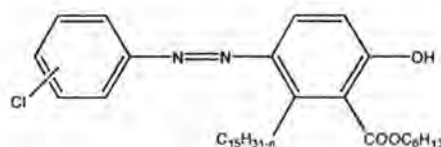
These marker dyes were synthesized by a coupling reaction of nitroanilines and esterified cashew nut shell extracted obtained from esterification reaction between cashew nut shell extracted and 1-hexanol. They could be used as marker dyes in gasoline and high-speed diesel at treat rates of 25 and 15 ppm, respectively. The detection of these markers in fuel oils was performed by extraction with 2% potassium hydroxide in ethylene glycol and gave clearly defined color in an extracted phase.

Suwanprasop, S. [22] synthesized the marker dyes for petroleum products which were synthesized by coupling reaction of cardanol, obtained from partially purification of decarboxylated cashew nut shell liquid, with diazonium salts of aniline derivatives. Their formulas were as follows.



These synthetic marker dyes were added into gasoline and high-speed diesel at levels of 2 to 5 ppm, and could be detected by extraction into 5% ethylenediamine in a solution of 1:1 ethylene glycol and methanol.

Thowongs, K. [23] synthesized the synthetic marker dyes for gasoline and diesel fuel having the formula:



These marker dyes were synthesized by esterification reaction between cashew nut shell extracted and 1-hexanol. Then, the esterified products were coupled with chloroanilines to give yellow color marker dyes. These marker dyes were used at treat rate of 30 ppm, and could be detected by extraction the tagged fuel oils with 10% of potassium hydroxide in methanol. These dyes gave yellow color in an extracted phase.