

## CHAPTER II

### THEORETICAL

#### 2.1 Color [4]

##### 2.1.1 Color Sensation

A Colored substance such as dye, when illuminated with white beam of light selectivity absorbs the particular part of the visible region (400 – 800 nm) and reflects the light of wavelengths in the rest of visible region. The color absorbed by a colored substance and color visualized are complimentary to each other. This relation is given in Table 2-1.

**Table 2-1** Color absorbed and color visualized with respect to wavelength region.

Wavelength (nm)	Color absorbed	Color visualized
400-435	Violet	Yellow-green
435-480	Blue	Yellow
480-490	Green-blue	Orange
490-500	Blue-green	Red
500-560	Green	Purple
560-580	Yellow-green	Violet
580-595	Yellow	Blue
595-605	Orange	Green-blue
605-750	Red	Blue-green

The absorption of the particular part of visible region by a given dye is the characteristic of its molecular structure, which depends upon the structural configurations of that dye. Therefore, the curve of absorption (y axis) against wavelength ( $\lambda$ ) (x axis), called as absorption spectra is unique and characteristic of that dye. The wavelength of absorption ( $\lambda$ ) is the quality and the molecular extinction coefficient (molar absorptivity) ( $\epsilon$ ) is the quantitative part. With the slight change in molecular structure the absorption curve changes with a shift in absorption wavelength (that is the maximum absorption wavelength peak) ( $\lambda_{max}$ ) or a change in the extinction coefficient ( $\epsilon$ ) or both. A shift of  $\lambda_{max}$  to regions of longer and shorter wavelengths are termed as bathochromic and hypsochromic effects respectively. Change in extinction coefficient indicates change in the intensity of visualized color.

### 2.1.2 Color and its relation to chemical constitution

Earlier worth theories such as Witt's theory, considered the organic colored compounds, *chromogens* (colourants) contain an unsaturated group fundamentally responsible for color and designated it as *chromophore*. Auxochromes are the characteristic groups, which intensify color and /or improve the dye affinity to substrate. Some of chromophores and auxochromes are given in Table 2-2.

Table 2-2 Chromophores and auxochromes

	<i>Linkage</i>	<i>Name</i>		
<i>Chromophores</i>	-N=N-	Azo		
	>C=S	Thio		
	-N=O	Nitroso		
	$\begin{array}{c} \oplus \\ -\text{N}=\text{N}- \\   \\ \text{O}\ominus \end{array}$	Azoxy		
	$\begin{array}{c} \text{O} \\ \diagup \\ -\text{N} \\ \diagdown \\ \text{O} \end{array}$	Nitro		
	-CH=N-	Azomethine		
	>C=O	Carbonyl		
>C=C<	Ethenyl			
<i>Name</i>		<i>Group</i>	<i>Name</i>	<i>Group</i>
<i>Auxochromes</i>	Amino	-NH <sub>2</sub>	Chloro	-Cl
	Methylamino	-NHCH <sub>3</sub>	Methyl	-CH <sub>3</sub>
	Dimethylamino	-N(CH <sub>3</sub> ) <sub>2</sub>	Methoxyl	-OCH <sub>3</sub>
	Sulphonic acid	-SO <sub>3</sub> H	Cyano	-CN
	Hydroxy	-OH	Acetyl	-COCH <sub>3</sub>
	Carboxylic acid	-COOH	Amido	-CONH <sub>2</sub>

The inconsistencies and inadequacy of the chromophore-auxochrome theory long have been recognized. Hence the modern concepts in the terms of electronic energy have been discussed. When a colored substance illuminated with white beam of light absorbs a part of it, causing electronic energy changes and the molecule is raised from the ground state energy  $E_0$  to the excited state  $E_1$ , the difference  $\Delta E$  is the quantum of energy given by quantum theory equation (2.1).

$$\Delta E = E_1 - E_0 = h\nu = hc/\lambda \quad \dots(2.1)$$

Where,  $\nu$  = frequency,  $\lambda$  = wavelength of absorption,  
 $h$  = Planck's constant,  $c$  = velocity of light.

In multiple double bonds of an unsaturated compound such as dye where the electron is much more mobile the values of  $\Delta E$  lie between 71 and 35.5 kcal per mole as we pass from 400 nm to 800 nm. Thus, the absorption of electronic energy will occur in a particular region of visible range.

The modern theory correlating the color and chemical constitution of dyes is based on establishing the relation between quantum mechanical calculations of absorption of light involving atomic orbitals and molecular orbitals with observed absorption spectra of the dye. There is an important conclusion that the molecule of dye is considered as having a *Resonance hybrid* of the possible structures and resonance hybrid is more stable than any of the individual structures. The difference in the energies at excited state and ground state of the hybrid becomes lesser. Therefore, absorption will shift towards longer wavelength as the space available for  $\pi$  electron in which it is free to move becomes larger.

## 2.2 Dye and Marker

### 2.2.1 Dye

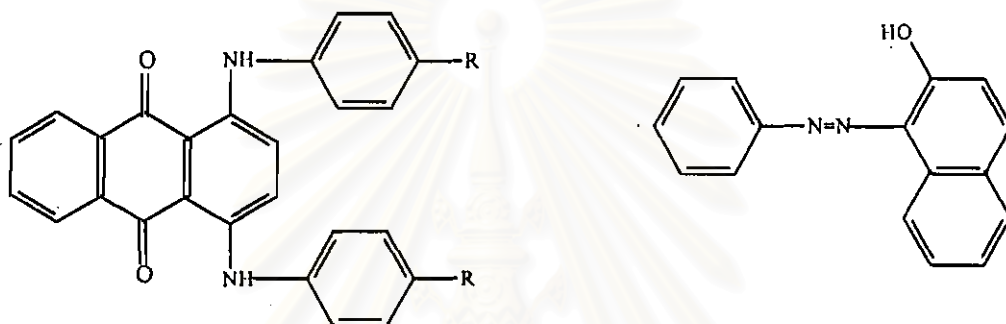
A dye may be defined as an organic compound used to impart color to other substances. It has necessarily retaining power properly on the substance to retain its color on prolonged exposure to light or to resist removal under conditions to which the substance normally is exposed [5].

Dyes used for coloring petroleum products, such as, gasoline, kerosene, are carried out in order to render them identifiable, and thus make difficult the possible tax evasions, which can result from utilizing said products for purpose that differ from the ones for which they are taxed. These dyes must satisfy various requirements as the following [6]:

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

10. to must primarily be extractable with difficulty from the system in which it is dissolved.

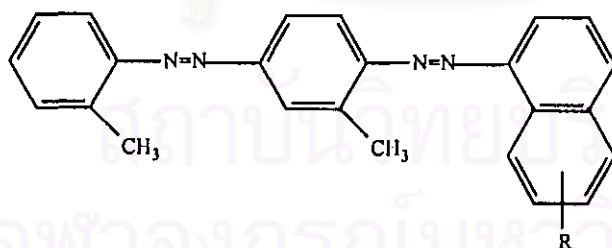
Examples of oil-soluble dyes were shown as the following [5, 6, 7]:



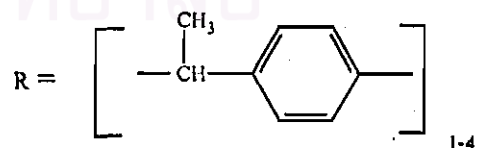
Where R = H, CH<sub>3</sub>

Solvent Yellow 14 (Sudan I, 747)

Solvent Blue 76, Solvent Green 3/C.I.61565



Red dye



### 2.2.2 Marker

A marker is defined as a substance, which can dissolve in a liquid to be identified then detected by performing a simply chemical or physical test on the marked liquid. Markers which are in use, include furfural, quinizarin, diphenylamine, various naphthol derivatives, and radioactive materials.

Markers for petroleum products should possess the following properties:

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

Dyes and markers are needed to clearly distinguish chemically or physically similar liquid. Many dyes are easily removed by unauthorized persons. Furthermore, dyes can be obscured by other natural or added substances (particularly dyes present at low concentrations in a mixture of fuels). Therefore dyes alone are not always to securely and reliably identify liquids. A combination of dye and a marker is used to tag an organic liquid [1, 8].

### 2.2.3 Azo dye

The azo dyes constitute the largest and most varied group of synthetic organic dyes in use today. They are compounds containing azo group (-N=N-) which are linked to sp<sup>2</sup>-hybridized carbon atoms and prepared by coupling a diazotized aromatic amine, the *primary* component, with a phenol or an aromatic amine, the *secondary* component [5]. There are two reactions in the synthesis of azo dyes.

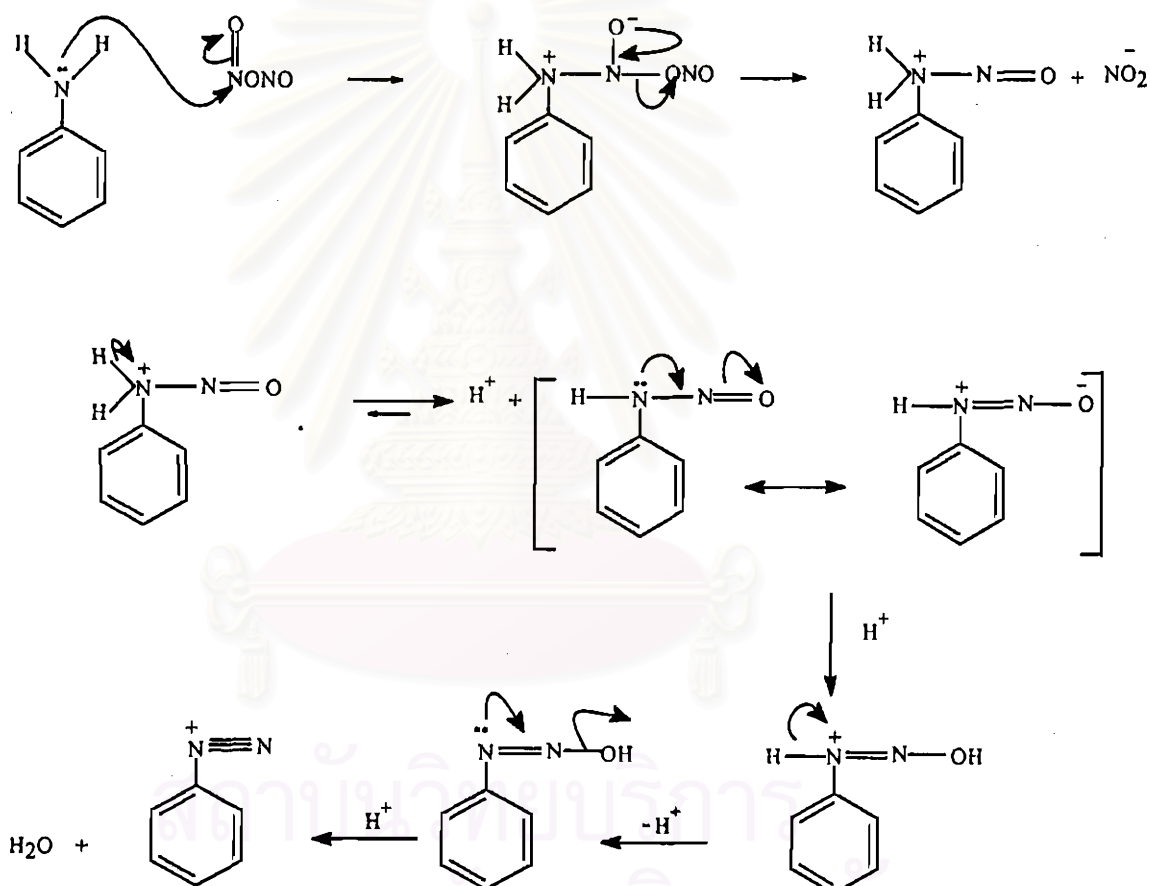
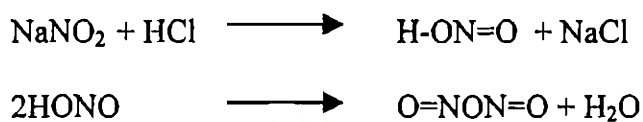
#### 1. Diazotization [9, 10]

Aromatic primary amines react with sodium nitrite in the presence of mineral acid (usually HCl, H<sub>2</sub>SO<sub>4</sub>) at a temperature of about 0 – 5 °C to form the diazonium salt. The use of at least two (usually 2.5) equivalents of mineral acid is essential for smooth reaction. One equivalent is needed to generate nitrous acid from sodium nitrite, one equivalent is needed to convert the diazonium hydroxide to the diazonium cation and the rest equivalent is needed to repress a complicating reaction that always awaits the unwary chemist in a diazotization - the coupling of the diazonium cation formed with unreacted aromatic amine produces diazoamino compound as the following equation.





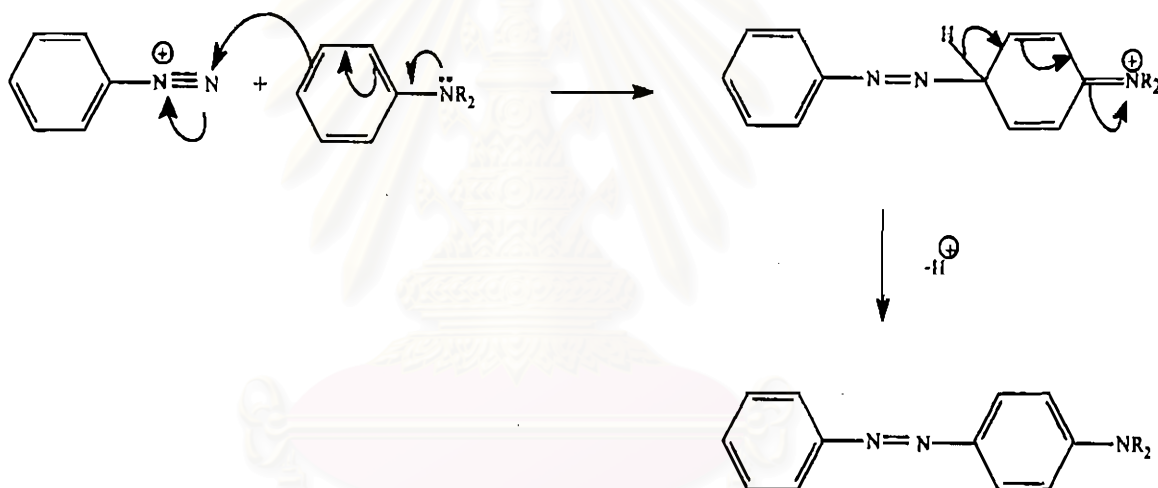
The diazotization reaction occurs according to the following equation [11].



## 2. Coupling Reaction

Diazonium salts undergo reaction with phenols in the presence of sodium hydroxide or with amines in the presence of sodium acetate, without loss of

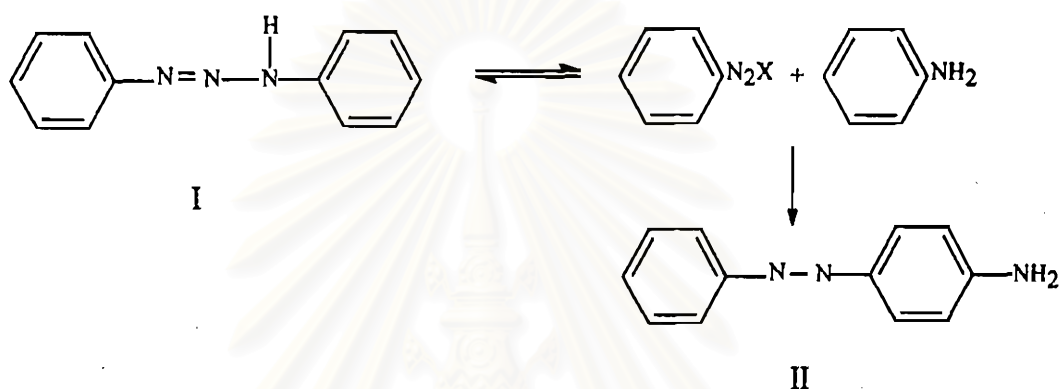
nitrogen, to produce azo dyes, known as coupling reaction. The coupling reaction is an electrophilic substitution involving the diazonium ion which reacts at the position of greatest electron availability to introduce azo group to para position of the hydroxyl or amino group if this position is unoccupied. If the para position is occupied, the azo group enters the ortho position, but never the meta position [12].



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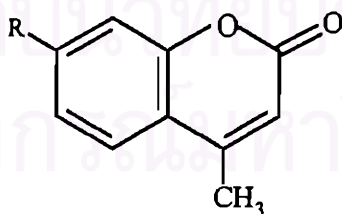
With primary and secondary amines the coupling reaction can also occur at the nitrogen atom to yield a diazoamino compound I as well as on the ring to form the aminoazo derivative II. Usually I forms more rapidly, but this reaction is reversible; II is more stable. Diazoamino compounds cannot form with tertiary

amines. Coupling reactions with amines are frequently carried out in buffered solutions [13].



### 2.3 Literature reviews

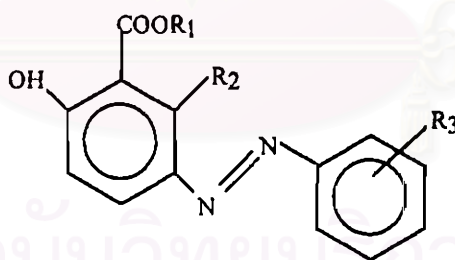
Friswell et al.[14] developed the silent fluorescent markers having the general formula:



where R is selected from a linear or branched  $\text{C}_1 - \text{C}_{18}$  alkyl carboxy radical.

These compounds are conveniently synthesized by esterification of an appropriately selected linear or branched  $C_1 - C_{18}$  alkyl carboxylic acid or acid halides with 7-hydroxy-4-methyl coumarin. Since these compounds have relatively higher solubility in organic liquids, that are particularly suitable as markers for liquid petroleum products and industrial liquids. The markers are used at level of about 0.25 ppm – 100 ppm. They can be detected in the products by extraction with an alkaline aqueous solution which produce extracts with deeply blue fluorescence when tested under a suitable source of light, such as an ultraviolet light emitting at 365 nm wavelength.

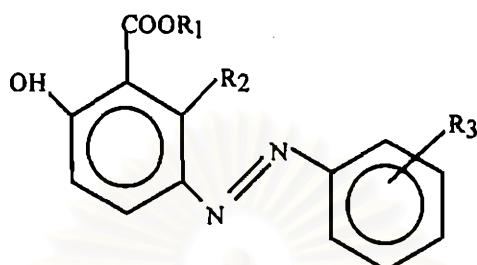
Silapakampeerapap.[2] developed the marker dyes having the general formula :



where  $R_1$  is  $C_6H_{13}$ ,  $R_2$  is  $C_{15}H_{25-31}$  and  $R_3$  is H or  $NO_2$

Markers in this research are conveniently synthesized by azo coupling of the ester of the cashew nut shell extract with nitroanilines. The markers are then added to liquid petroleum fuel at level of about 15-25 ppm. They can be detected by extraction with 2% potassium hydroxide in ethylene glycol

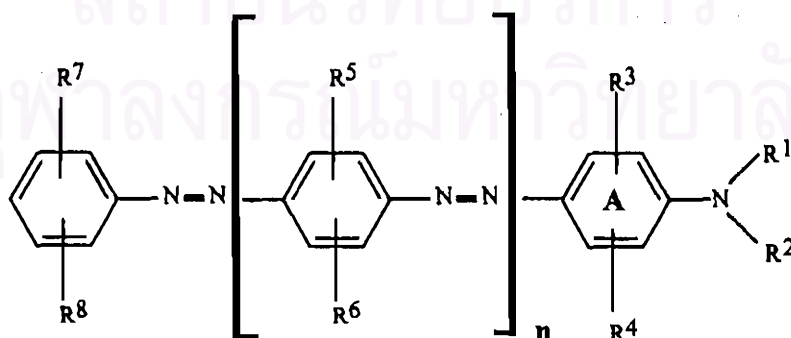
Thowongs.[3] developed the marker dyes having the general formula :



where  $R_1$  is  $C_6H_{13}$ ,  $R_2$  is  $C_{15}H_{25-31}$  and  $R_3$  is Cl

Markers in this research are conveniently synthesized by azo coupling of the ester of the cashew nut shell extract with chloroanilines. The markers are then added to liquid petroleum fuel at level of about 30 ppm. They can be detected by extraction with 10% potassium hydroxide in methanol which produce the yellow color in the extracted phase.

Zeidler et al.[15] developed the azo dyes as markers having the general formula:



where the ring A may be benzofused, n is 0 or 1,

$R^1$  is hydrogen or  $C_1 - C_{15}$  - alkyl, which may be interrupted by from 1 to 4 ether oxygen atoms,

$R^2$  is  $C_1 - C_{15}$  - alkyl, which may be interrupted by from 1 to 4 ether oxygen atoms,

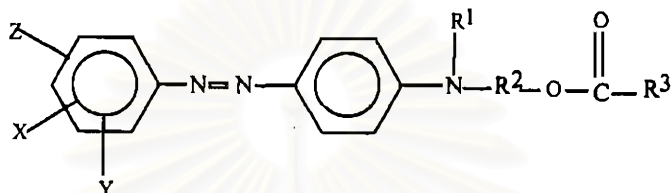
$R^3, R^4, R^5, R^6$  and  $R^7$  independently of one another are each hydrogen,  $C_1 - C_{15}$  - alkyl or,  $C_1 - C_{15}$  - alkoxy

$R^8$  is hydrogen,  $C_1 - C_{17}$  - alkyl,  $C_1 - C_{15}$  - alkoxy, cyano, nitro or a radical of the formula  $COOX^3$ , where  $X^3$  is hydrogen,  $C_1 - C_{15}$  - alkyl which may be interrupted by from 1 to 4 ether oxygen atoms,

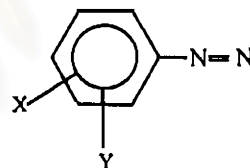
These azo dyes can be used as pH-dependent markers in particular mineral oil, such as gasoline, kerosine or diesel oil. The markerd fuels at level about 10 ppm or less are detected either with an aqueous alcoholic or alcoholic solution of a protic acid, with or without the addition of the metal halide, such as zinc chloride, aluminum chloride, or tin tetrachloride, in order to a color reaction, i.e. a color change, accompanied by a deepening of color. The volume of the extraction solution used from 10 to 50 ml is sufficient to extract from about 10 to 50 ml of marked fuel.

Friswell et al.[16] developed the petroleum fuel markers having the general formula:

5737871



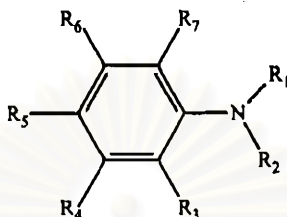
where  $R^1$  is  $C_1 - C_3$  - alkyl,  $R^2$  is  $C_1 - C_3$  - alkylene and  $R^3$  is  $C_1 - C_2$  - alkyl, preferably  $C_1$  alkyl, X and Y are the same or different and are selected from H, methyl, ethyl, methoxy, halogen and Z is H or



wherein X and Y are as defined above.

These compounds known as “solid dispersed dye” are synthesized in a mixed, two phase system in which the compounds disproportionate from an acidic aqueous phase into a solvent phase, providing petroleum fuel marker solutions. The tagged petroleum fuels at various levels from about 0.25 to 100 ppm are extracted with an acidic aqueous solution of an acid, such as HCl, phosphoric acid, formic acid, and propionic acid. Typically, the volume of acidic aqueous extraction solution to volume of fuel ranges from about 0.5:1 to about 10:1. The extracted phase produces color, which will be different, depending on the substituent groups.

Rainer et al.[17] developed the markers having the general formula:

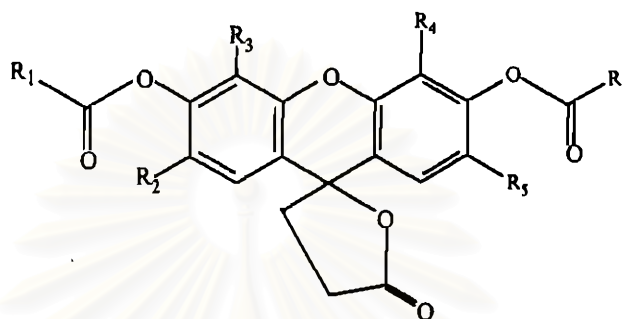


where  $R_1, R_2, R_3, R_4, R_5, R_6, R_7$  and  $R_8$  are each hydrogen, C1-C18-alkyl which is unsubstituted or substituted.

The anilines of the above formula used as markers in a concentration of about 10 ppm or less are particularly advantageously detected in mineral oil if the aniline of the above formula is extracted by treating the mineral oil with an aqueous solution of the diazonium salt which is derived from an amine from aminoanthraquinone series, and then coupled, with the diazonium salt, with formation of an azo dye, producing a strong color reaction and can be quantitatively detected by mean of photometric determination. Furthermore, the detection of the anilines of the above formula by means of a diazo paper or of a diazo film has proven advantageous.



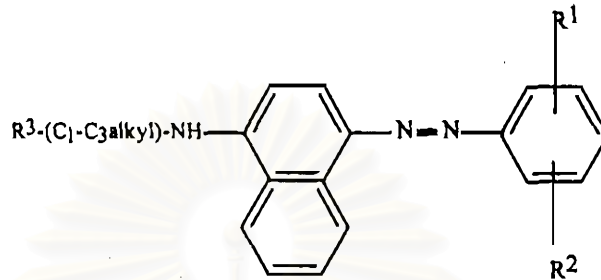
Smith et al.[18] developed the fluorescent petroleum markers having the general formula:



where  $R_1$  is an alkyl or aryl.  $R_2, R_3, R_4, R_5$  are  $-H, -Cl, -Br$  or  $C_1-C_{12}$  alkyl.

Compositions of the markers contain organic esters of fluorescent dyestuffs the hydroxyphthalein subclass of Xanthene dyes, which may be added to gasoline, diesel fuel, fuel oil, kerosene and lamp oil at levels of about 0.5 to about 100 ppm. These markers can be detected by extraction with the mixture of water aliphatic alcohols, glycols or glycol ethers and also quaternary ammonium hydroxide compounds. The extracted phase may be examined visually for the brilliant yellow to green fluorescence by irradiation with long-wave ultraviolet light and quantified by visible light absorption spectrophotometry or by spectrofluorimetry.

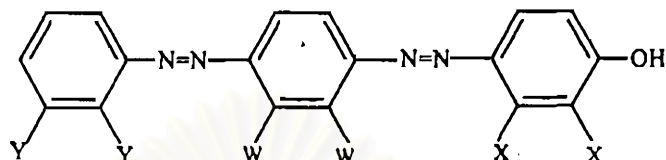
Friswiell et al.[19] developed the petroleum fuel markers having the general formula:



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 in this patent are conveniently synthesized by azo coupling of an appropriately substituted aniline with an alpha-naphthylaniline. The markers are then added to liquid petroleum fuel at level of about 0.25 ppm or above. They can be detected by extraction with 10-30% aqueous solution of an acid, such as hydrochloric, formic acid and phosphoric acid, Typically the volume ratio of extraction mixture to liquid petroleum fuel is between about 1:1 and about 1:40. Colorimeter equipment may be used to quantify the amount of marker in the aqueous layer.

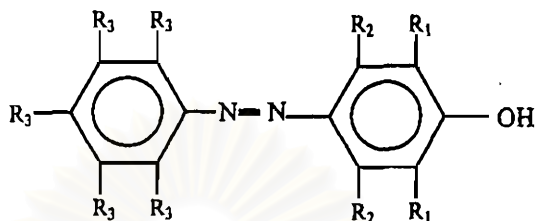
Hallisy et al.[20] developed the markers having the formula:



where the Ws are selected from O—(C1-C3 alkyl) and hydrogen, provided that at least one W is O—(C1-C3 alkyl), the Xs and Ys are the same or different and are select from hydrogen, alkyl, substituted alkyl, alkenyl, substituted alkenyl, aryl, substituted aryl, fuse aryl, substituted fused aryl, halogen, nitro, cyano and alkoxy.

These markers are conveniently synthesis by azo coupling of an appropriately substituted aniline to a phenol, such as 2,6-di-sec-butyl phenol. They are added to liquid petroleum product at level of about 5-40 ppm. The markers can be detected by extraction with an alkaline aqueous medium, for example 2% of NaOH in 50% aqueous methanol. Typical the volume ratio of extraction mixture to liquid petroleum product is between 1:1 and about 1:40. Colorimeter equipment may be used to quantify the amount of marker in the aqueous layer.

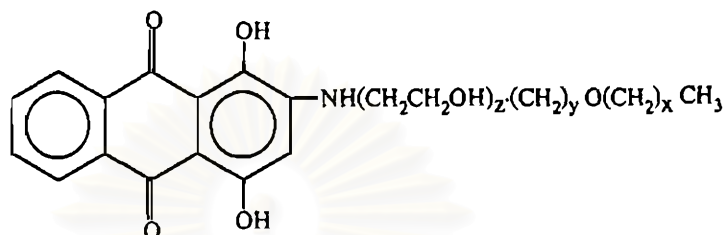
Friswell et al.[21] developed the silent markers having the formula:



where the R<sub>1</sub>'s and R<sub>2</sub>'s are each selected from hydrogen and C1-C7 alkyls. R<sub>3</sub>'s are selected from -H, -NO<sub>2</sub>, -Cl, -Br, -F, -CN and -Me.

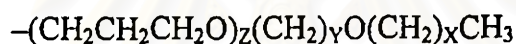
These marker compounds are synthesized by azo coupling of an appropriately substituted aniline to a 2,6-dibutyl phenol (preferably a 2,6-disecbutylphenol). They are added to liquid petroleum product at levels of about 0.25 ppm or above. They can be detected by extraction with a reagent comprising water and a water-soluble amine, such as methoxy propyl amine methoxy ethoxy propylamine and, preferably a water-miscible co-solvent, such as, ethyl alcohol, ethylene glycol, propylene glycol. Typically the volume ratio of extraction mixture to liquid petroleum is between about 1:1 and about 1:10. Colorimeter equipment may be used to quantify the amount of marker in the aqueous layer.

Orelup et al.[22] developed the markers having the formula:



wherein R is an alkyl moiety selected from the group consisting of

(1) moieties having the following structure



wherein X is an integer between 0 and 3 inclusive, Y is an integer between 1 and 3 inclusive, Z is 0 or 1.

(2) linear or branched hydrocarbons having from 1 to about 5 carbon.

Two methods for detecting markers consist of (1) extraction with a reagent comprising glycerine, water and an organic amine. A substantially bluish red or red color is produced in an aqueous layer. (2) passing a marked fuel through an activated alumina chromatographic column. A substantially purple zone of tagging compound is formed in said column. Absorbance of the colored solution is measured instrumentally and related to marker concentration.