

## CHAPTER II

### THEORY

#### 2.1 Marker Dyes

Marker dyes [1,2,3,4] of the present invention are suitable in particular for marking mineral oils that have to be marked for tax purposes. To keep the costs of marking to a minimum, it would be desirable to use dyes of very high color strength. However, these strong dyes are no longer perceivable purely visually when present in high dilution in mineral oils.

Using the marker dyes it is a very simple matter to detect marked mineral oils, although a concentration of the marking substances are present only approximately 5 ppm in mineral oils. Dye and markers are needed to clearly distinguish chemically or physically similar oils. Besides the commercial and safety reasons, fuels are dyed to provide visually distinctive brand and grade designations. In addition, some highly taxed products are tagged to distinguish them from similar materials subject to less taxed products.

Furthermore, certain fuels are dyed or marked to detect fraudulent adulteration of premium grade products with lower grade products, such as by blending kerosene, stove oil, or diesel fuel into regular grade gasoline or blending regular grade gasoline into premium grade gasoline.

Identification of particular batches of bulk liquids for protection against theft is another valuable function of markers and dyes, particularly for identifying fuels owned by large government, military or commercial consumers.

Dyes can be obscured by other natural or added substances because dyes alone have these shortcomings, a combination of a dye and a marker often is used to tag an organic liquid. Therefore, dyes alone are not always adequate to be used securely and reliably as tag liquids because unauthorized persons easily detect many dyes.

The objects fulfilled by this invention are to provide novel tagging compounds for petroleum fuels and other liquids which:

1. Are entirely foreign to the liquids.
2. Can be provided as highly concentrated solutions in compatible solvents.
3. Are easily detected by a simple field test.

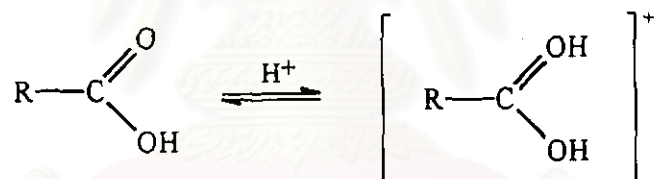
4. Have identified which can be confirmed by laboratory methods.
5. Are not obscured by unstable natural components of the liquids.
6. Are stable over the anticipated storage life of the tagged liquid.
7. Act as both a marker and a dye by simultaneously imparting an acceptably intense red color and functioning as a marker at low concentration in the tagged liquid.

## 2.2 Esterification

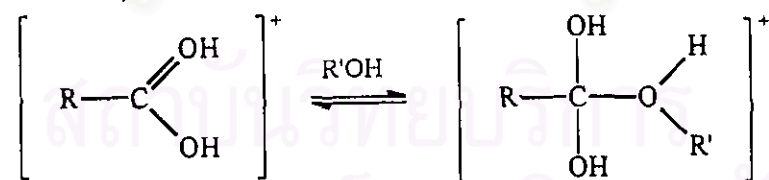
Esters may be prepared by direct esterification of an acid with an alcohol in the presence of an acid catalyst (sulfuric acid, hydrogen chloride) and by alcoholysis of acid chlorides, acid anhydrides, and nitriles. Occasionally they are prepared by heating the metallic salt of a carboxylic acid with an alkyl halide or alkyl sulfate.

Direct esterification is an acid-catalyzed nucleophilic addition of an alcohol to the carboxyl group of an organic acid. The reaction occurs through the following mechanism, illustrated with acetic acid and ethanol:

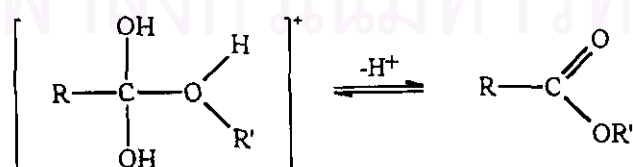
- (1) Protonation of the carboxyl group.



- (2) Addition of the alcohol and shift of its proton to one of the hydroxyl groups.



- (3) Elimination of water and deprotonation.



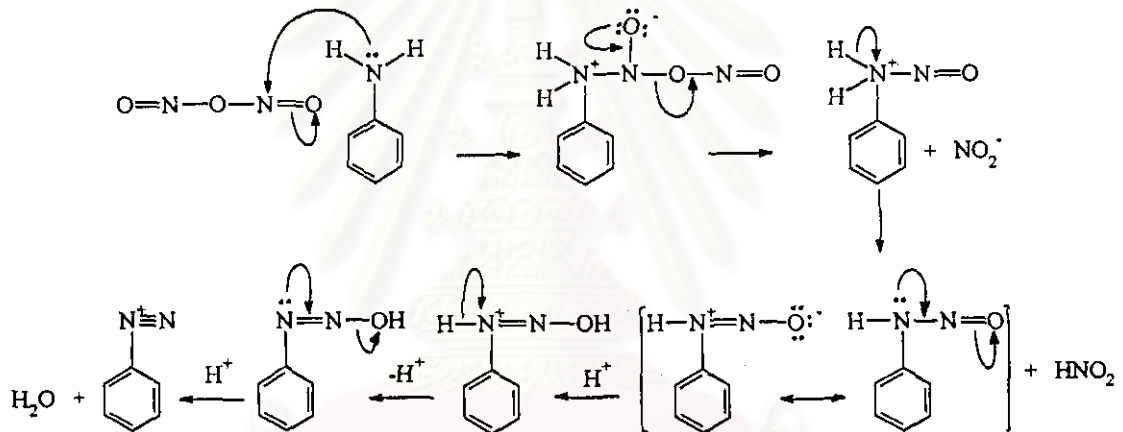
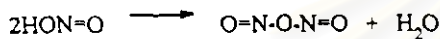
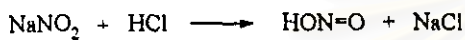
It has been demonstrated that an oxygen atom of the carboxyl group is eliminated as water and the oxygen atom of the alcohol is retained in the ester. Since the reaction is reversible, the equilibrium must be shifted forward to obtain good conversion to the ester. The use of an excess of one of the initial reactants, removal of one of the products or a combination of both serves this purpose. [5]

### 2.3 Diazotization

This is a reaction between a primary aromatic amine and nitrous acid to give a diazo compound. Diazotization is an important reaction in organic chemical synthesis.

#### Preparation of Diazonium Salts

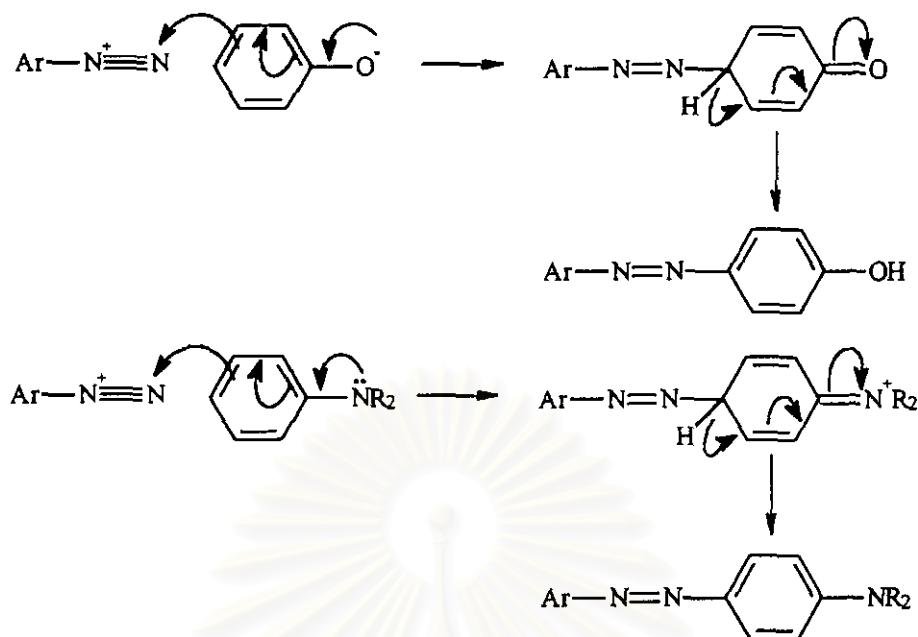
The direct method is by slow addition of an aqueous solution of sodium nitrite to a solution of amine in dilute mineral acid held at 0-10°C. Excess mineral acid, usually about 2.5 moles, is used to prevent formation of diazoamino by-product, and since the reaction is exothermic, cooling is required to maintain a temperature at which the diazo product is stable. [6]



Scheme 1.1 The mechanism of diazotization.

### 2.4 Coupling Reaction

Coupling of diazo compounds with phenols, naphthols, amines and certain other components to form azo dyes is the basis of their most important commercial use. The most probable mechanism is by attack of the strongly electrophilic diazonium ion on a position of high electron density in a nucleophilic coupling component. With phenols the greater electron density at the para position in the phenolate ion aids coupling unless the pH becomes so high that the diazonium salt is substantially converted to the noncoupling isodiazolate. Coupling with amines occurs more readily near the neutral point than at lower pH where amine salt is present. [6, 7]



**Scheme 1.2** The mechanism of coupling reaction.

## 2.5 The Ultraviolet and Visible Absorption Spectrum

Light of wavelength between about 400 nm and 750 nm is visible. Just beyond the violet end of the visible spectrum ( $\lambda$  less than 400 nm) lies the ultraviolet region.

The ultraviolet spectrometers commonly used to measure absorption of light in the visible and “near” ultraviolet region, that is, in the 200-750 nm range. This light is of higher frequency (and greater energy) than infrared light and, when a molecule absorbs it, the changes it produces are, naturally, ones that require greater energy: changes in electronic states.

In a transition to a higher electronic level, a molecule can go from any of a number of sub-levels, corresponding to various vibrational and rotational states, to any of a number of sub-levels; as a result, ultraviolet absorption bands are broad. Where an infrared spectrum shows many sharp peaks, a typical ultraviolet spectrum shows only a few broad humps. One can conveniently describe such a spectrum in terms of the position of the top of the hump ( $\lambda_{\text{max}}$ ) and the intensity of that absorption ( $\epsilon_{\text{max}}$ , the extinction coefficient).

The electronic transitions of most concern to the organic chemist are: (a)  $n \rightarrow \pi^*$ , in which the electron of an unshared pair goes to an unstable (anti-bonding)  $\pi$

orbital. (b)  $\pi \rightarrow \pi^*$ , in which an electron goes from a stable (bonding)  $\pi$  orbital to an unstable  $\pi$  orbital.

A  $\pi \rightarrow \pi^*$  transition can occur for even a simple alkene such as ethylene but absorption occurs in the far ultraviolet, which cannot be easily detected. Conjugation of double bonds, however, lower the energy required for the transition, and absorption moves to longer wavelengths, where it can be more conveniently measured. If there are enough double bonds in conjugation, absorption will shift into the visible region, and the compound will be colored. [8]

## 2.6 Extraction

Extraction is the separation method that involves the transfer of a substance from one material phase into a second phase. When the two phases are immiscible liquids, this method is known as a liquid-liquid extraction. In liquid-liquid extractions a compound is partitioned between two solvents. The successes of the separation depend on the difference in the solubilities of the compound in the two solvents. Generally the compound that is to be extracted is insoluble or only partially soluble in one solvent but is very soluble in the other solvent.

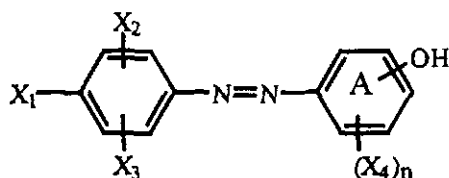
Acid-base extractions are generally employed for the isolation of covalent acids from organic mixtures by procedures that will use to isolate covalent acids. Similarly, covalent bases are isolated from organic mixture by extractions with aqueous mineral acid; the base is isolates after treating the aqueous solution that contains the conjugate acid of the covalent base with aqueous with aqueous sodium hydroxide. [9]

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

## 2.7 Literature Reviews

US Patent 5,487,770 "Detection of marked mineral oils and novel azo dyes" [10]

The general formula of azo dyes were used to mark mineral oils in this invention.

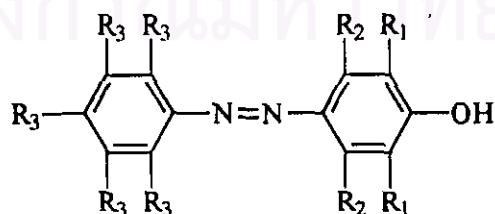


The ring A may be benzofused and n is from 1 to 4. The X<sub>1</sub>, X<sub>2</sub> and X<sub>3</sub> are hydrogen, C<sub>1</sub>-C<sub>4</sub>-alkyl, cyano or nitro, provided that at least one, and preferably both the X<sub>2</sub> are C<sub>1</sub>-C<sub>4</sub>-alkoxy or C<sub>1</sub>-C<sub>16</sub>-alkoxycarbonyl. The X<sub>4</sub> is hydrogen, hydroxyl, substituted or unsubstituted C<sub>1</sub>-C<sub>8</sub>-alkyl, C<sub>1</sub>-C<sub>4</sub>-alkoxy, amino, C<sub>1</sub>-C<sub>4</sub>-dialkylamino or substituted or unsubstituted C<sub>1</sub>-C<sub>16</sub>-monoalkylamino.

A Method for detecting azo dyes marked mineral oils was carried out by treating the marked mineral oil with an extractant comprising water, a partially or completely water-miscible organic solvent, an alkali or alkaline earth metal hydroxide, and an alkali metal carbonate or an ammonium compound. When the marked mineral oil was shaken with extraction solvent, the azo dye could transfer into the aqueous phase and then it appeared a visible color such as yellow, orange, red or violet. This azo dye was added only in a concentration of about 10 ppm or less as marker in mineral oils.

US Patent 5,156,653 "Silent markers for petroleum, method of tagging, and method of detection" [11]

Markers of this invention were phenylazophenols derivatives having general formula below.



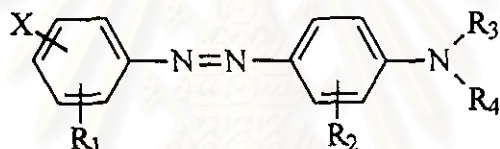
The R<sub>1</sub>'s and the R<sub>2</sub>'s are the same or different and each are selected from -H and C<sub>1</sub>-C<sub>7</sub>alkyls, provided that at least one, and preferably both R<sub>1</sub>'s are a C<sub>3</sub>-C<sub>7</sub> alkyl. The R<sub>3</sub>'s are the same or different and are selected from -H, -NO<sub>2</sub>, -Cl, -Br, -F, -CN,

and -Me; and provided that at least one  $R_3$  is selected from  $-\text{NO}_2$ ,  $-\text{Cl}$ ,  $-\text{Br}$ ,  $-\text{F}$ , and  $-\text{CN}$ .

Markers at level of about 0.25 ppm or above (usually at least about 1 ppm) were added to liquid petroleum products and were detected by extractant. These reagent systems, that were a reagent comprising water, water-soluble amine and water-miscible co-solvent, extracted the marker from the liquid petroleum product, providing a clearly defined color developed in an aqueous phase. The volume ratio of extraction mixture to liquid petroleum was between about 1:1 and about 1:10. In addition to colorimetric equipment may be used to quantify the amount of marker in the aqueous layer.

US Patent 5,266,227 "Oil-soluble phenylazoaniline dyes" [12]

Phenylazoaniline dyes were used for marking mineral oils.

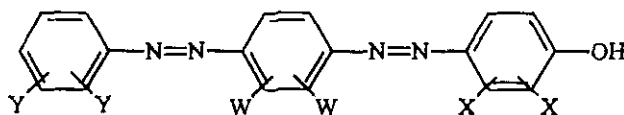


The  $R_1$  and  $R_2$  were  $-\text{H}$ ,  $\text{C}_1\text{-C}_4$  -alkyl or  $\text{C}_1\text{-C}_4$  -alkoxy. The  $R_3$  was  $-\text{H}$  or  $\text{C}_1\text{-C}_8$  -alkyl which may be substituted by hydroxyl, and interrupted by from 1 to 3 oxygen atoms.

These azo dyes were obtained from diazonium salts and coupling components both belong to the aniline series and where the radical of the diazo component derived from an aminobenzoic acid derivatives. The markers may be detected by shaking with mixture of suitable solvents such as toluene or xylene, and aqueous mineral acids such as hydrochloric acid, sulfuric acid or aqueous alcoholic hydrochloric acid in a concentration of approximately 3-20% by weight, preferably 5-10% by weight. These markers were added only in a concentration of approximately 0.1 ppm into fuel.

US Patent 5,252,106 "Base extractable petroleum markers" [3]

Liquid petroleum products are tagged with a marker of the general class of chemicals describes as phenylazophenols

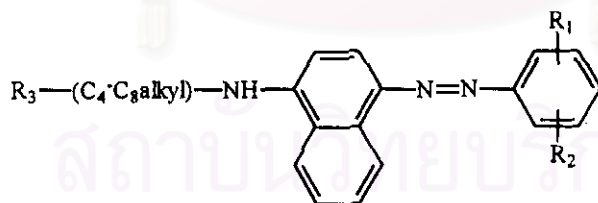


The Ws are selected from O-(C<sub>1</sub>-C<sub>3</sub> alkyl) and hydrogen, provided that at least one W is O-(C<sub>1</sub>-C<sub>3</sub> alkyl), the Xs and Ys are the same or different and are selected from hydrogen, alkyl, substituted alkyl, alkenyl, substituted alkenyl, aryl, substituted aryl, fused aryl, substituted fused aryl, halogen, nitro, cyano, and alkoxy.

Markers at levels of about 0.25 parts per million (ppm) or above (usually at least about 1 ppm) are added to liquid petroleum products. The markers may be detected in the petroleum products by extraction with an alkaline aqueous solution, such as 2.5% NaOH in 50% aqueous methanol. Colorimetric equipment may be used to quantify the amount of marker in the aqueous layer. For a rough estimate of marker level, the inspector might even be provided with a color chart against which to compare the developed color.

US Patent 5,490,872 "Acid extractable petroleum markers" [4]

Petroleum fuels are tagged with markers having the formula



The R<sub>1</sub> and R<sub>2</sub> are selected from H, methyl, ethyl, methoxy, halogen, cyano and nitro while R<sub>3</sub> is selected from methyl, methoxy, methoxyethoxy and morpholino.

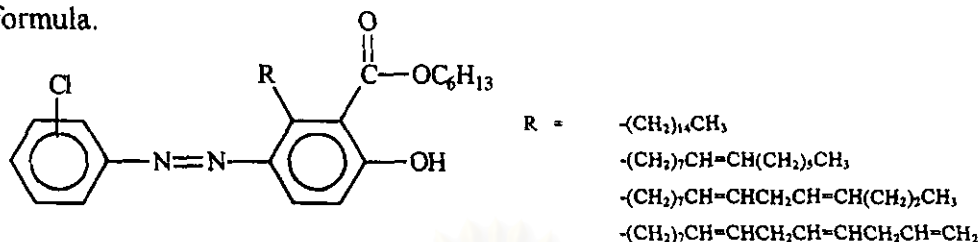
Markers at levels of about 0.25 parts per million (ppm) or above (usually at least 1 ppm) are added to liquid petroleum fuels. The markers may be detected in the petroleum fuels by extraction with an acid aqueous solution, such as HCl, formic acid, and phosphoric acid. The extraction solution may also include a water-miscible, petroleum-miscible organic solvent, such as methanol. The volume ratio of extraction mixture to liquid petroleum is between about 1:1 and about 1:40.



## Thesis "Marker dye from cashew nut shell extract and chloroanilines" [13]

Kitipol Thowongs.

The marker dyes, which were added into high speed diesel and gasoline had the formula.

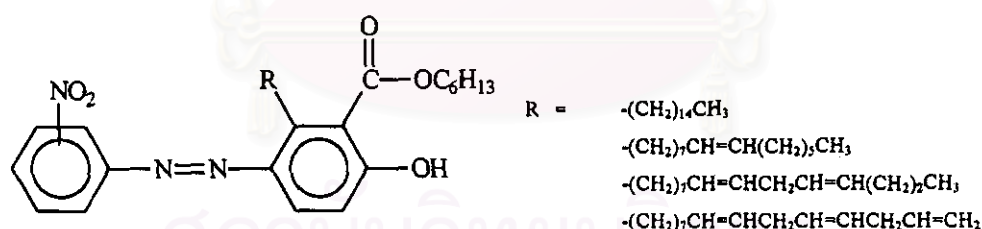


The extracted cashew nut shell liquid was esterified by hexanol and coupling with diazonium salt of aromatic amines, which had chlorine-substituent in different position, to obtain yellow-color markers as the product. The marker was added to petroleum products at levels 30 ppm and was extracted from the petroleum products with 10% KOH in methanol. The characterization of marker dyes from both reactions was assisted by spectroscopic technique.

## Thesis "Marker dyes from cashew nut shell extract and nitro anilines" [14]

Supap Silapakampeerapab.

The synthesis of azo compounds, which had marker and dye properties in petroleum oils, had the formula.



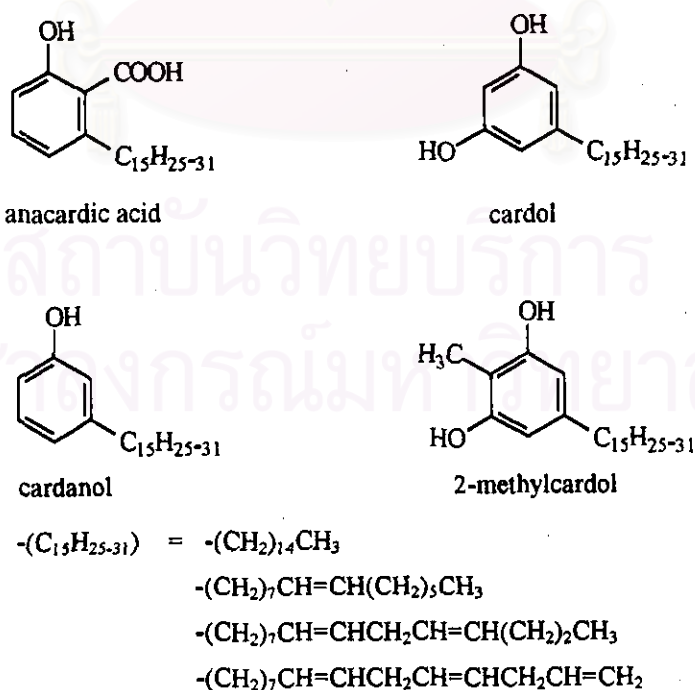
These marker dyes gave yellow color when mixed with oil and can be extracted to give different colors. The cashew nut shell extract was esterified with 1-hexanol to block the remaining carboxylic acid moiety. The azo dyes thus obtained were added into petroleum oils at level 25 ppm to give yellow color. The color of *m*-nitroaniline azo dye after extracted with glycolic potassium hydroxide solution was yellow color while the azo dyes prepared from *o*-nitroaniline and *p*-nitroaniline, gave orange and red color in aqueous phase, respectively. Properties of azo dyes, quality and quantity of dyed oils, were determined by colorimetric equipment.

## 2.8 Cashew Nut Shell Liquid

Cashew Nut Shell Liquid (CNSL) is contained in the honeycomb structure between the soft outer skin of the nut and the harder inner shell. It is a dark brown viscous liquid and is reported to occur in the fresh shell to the extent 15 to 20 and 20 to 30 per cent by weight for African nuts and Indian nuts, respectively. [15, 16]

CNSL, is mixture of phenolic compounds, consists of two principal compositions, anacardic acid and cardol. Both belong to the group of chemicals classified as higher phenols. In its natural state, the composition of CNSL is shown in Scheme 1.3. In each fraction, it has a side chain of 15 carbon atoms with different degree of unsaturation (Scheme 1.3). [15, 17, 18, 19]

Anacardic acid readily loses carbon dioxide to yield a meta-substituted phenol, "cardanol" on heating. For commercial usage the CNSL is obtained from the cashew nut shell by a process that involves heating the shells to a high temperature for several minutes in a vat of previously obtained the liquid. During this process the liquid 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 contains a small amount (approximately 16%) of anacardic acid, cardol and polymerized material.



Scheme 1.3 Composition of naturally occurring CNSL [15]