

CHAPTER II

THEORETICAL

2.1 Color of substances

Coloration of organic compounds is arisen from electronic excitation of a molecule caused by absorption of energy from irradiating white light. Only the molecules containing unsaturation or non-bonded electrons can absorb light in the visible region (400-800 nm) in such a way that some wavelengths are removed from ordinary white light, and only the remainders reach the eyes [5]. In general, the visual color is complementary to the color absorbed as indicated in Table 2-1 [6].

Table 2-1: The relation between color absorbed and visual color of a molecule.

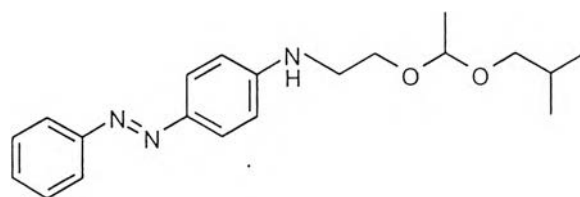
Wavelength absorbed (nm)	Colored absorbed	Visual color
400 – 435	Violet	Yellow-green
435 – 480	Blue	Yellow
480 – 490	Green-blue	Orange
490 – 500	Blue-green	Red
500 – 560	Green	Purple
560 – 580	Yellow-green	Violet
580 – 595	Yellow	Blue
595 – 605	Orange	Green-blue
605 – 750	Red	Blue-green

In 1876, Witt found that two types of groups are usually presented in colored compounds. unsaturated groups, which were called "chromophore", and groups that intensified the color, which were called "auxochrome". Examples of chromophore are NO_2 , $\text{C}=\text{O}$, $\text{N}=\text{N}$, $\text{C}=\text{C}$, $\text{C}=\text{N}$, $\text{C}=\text{S}$, $\text{N}=\text{O}$, and quinonoid structure. The important auxochromes are the hydroxyl group, the amino group, and the alkylated amino group. In general, when the molecules contain extended series of conjugated multiple bonds; they will absorb light at longer wavelength than those with only a few conjugated multiple bonds. This effect is called "Bathochromic shift" or "Red shift" [7].

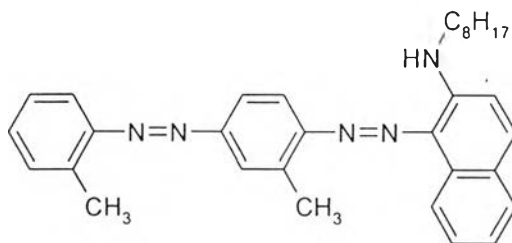
2.2 Azo dyes

A dye is defined as an organic material giving visible color when dissolves in dyed product. Thus, a fuel containing an organic dye immediately provides information to an observer. The red dye, Red-26, and yellow dye, Solvent Yellow-124, are the examples of organic dyes used in petroleum products.

Solvent Yellow-124 dye:



Red dye:



Dyes are used as coloring agents in industrial organic solvents, and of the petroleum products such as gasoline, kerosene, and diesel fuel. The coloring materials must satisfy various requirements as follows [8]:

- 1) To possess a high dyeing power
- 2) To have a sufficient solubility in organic solvents and fuel oils, in the presence or absence of antiknock agents
- 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 no powders in the solid form
- 9) To be sufficiently fluid to be solubilized in organic solvents, if it is used in the form of concentrated solution.

The use in the form of concentrated solution allows many advantages, when comparing with powdery products, such as convenient to use, rapidity of dosage, high diffusion coefficient, and absence of powders.

2.3 Marker dyes

A marker is defined as a substance, which can be used to tag petroleum products for subsequent detection, and is colorless in the petroleum products. The marker is dissolved in a liquid to be identified, then subsequently detected by performing a simple chemical or physical test on the tagged liquid [9].

The important characteristics of desirable markers for petroleum products include [10]:

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

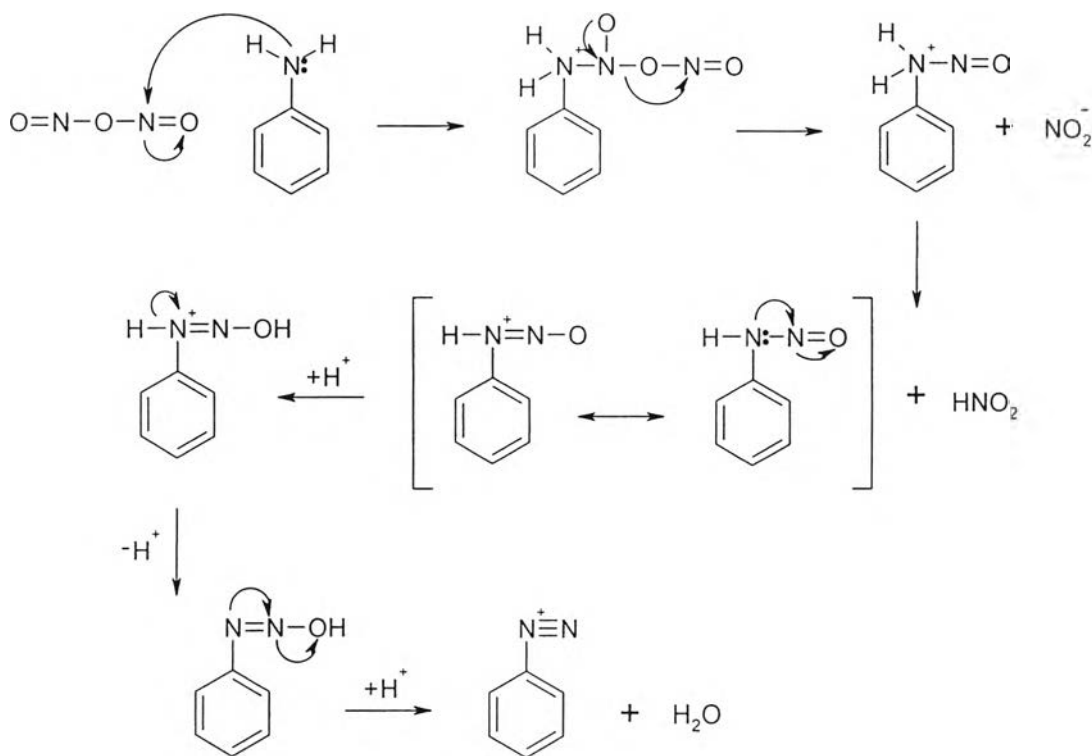
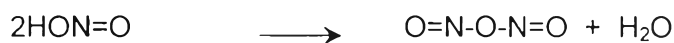
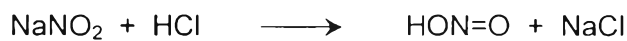
Dyes and markers are used for the purpose of distinguishing chemically or physically similar liquids, but dyes alone are not always adequate to securely and reliably identify liquids. Many dyes are easily removed from the products by unauthorized person. Moreover, many dyes can be obscured by other substances in the liquid. Because dyes alone have these disadvantages, a combination of dyes and marker is used to tag liquid petroleum products.

2.4 Preparation of azo dye

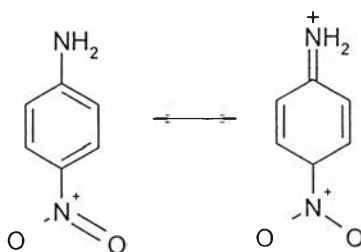
Azo dyes are prepared by coupling a diazotized aromatic amine, the primary component, with a phenol or an aromatic amine, the secondary component. Since many diazonium ions decompose rapidly in solution, it is necessary to conduct the azo dye synthesis under deep cold conditions, and use freshly prepared diazonium ions.

2.4.1 Diazotization of aromatic amine

The diazotization of primary aromatic amines is normally carried out by adding an aqueous solution of sodium nitrite to a solution of the amine hydrochloride in an excess of hydrochloric acid, which is cooled in an ice bath. The rate of addition is controlled so that the temperature of the reaction remains below 5 °C, addition is continued until the solution just contains an excess of nitrous acid. The mechanism of reaction may be summarized as follows:



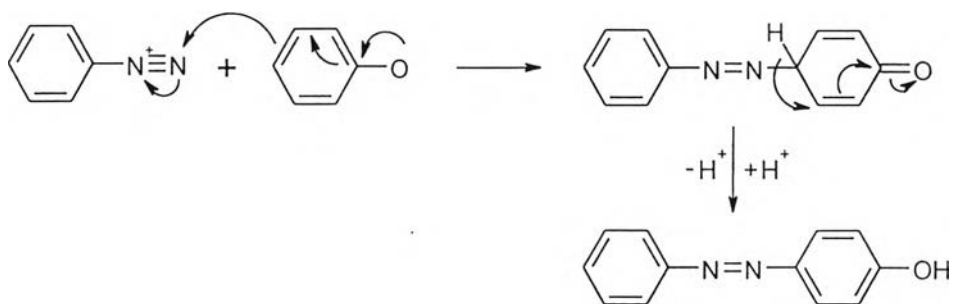
Aromatic amine, which is substituted in an aromatic ring with the electron-withdrawing groups, is less easy to diazotize, because the nucleophilicity of the amino-nitrogen is reduced by the partial withdrawal of the unshared electron pair into the ring, e.g.



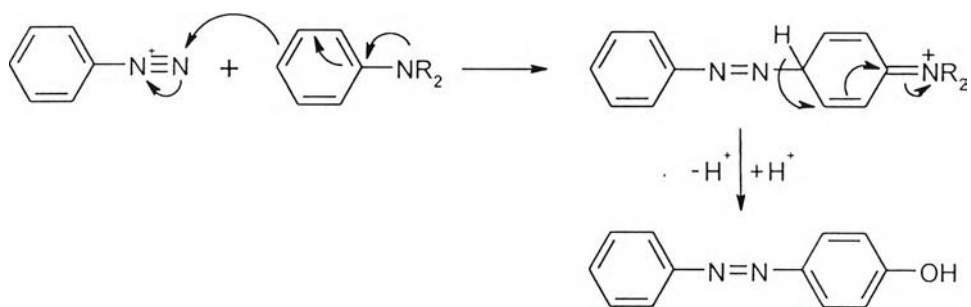
In this instance, only high concentration of acid is a suitable reaction medium [11].

2.4.2 Coupling reaction of phenol and diazotized aromatic amine

The coupling of diazonium ion with phenol occurs *via* the phenoxide ion. It is therefore necessary to carry out the reaction in an alkali solution, and caution must be taken to prevent the conversion of the diazonium ions into the diazohydroxides [11]. The optimum pH for coupling is about 9 to 10, but it is common to add an acidic solution of the aqueous diazonium ions to a solution of the phenoxide ions in sufficient amounts of alkali to neutralize the acids formed, and to maintain suitable alkalinity. Coupling reaction occurs rapidly to prevent destruction of the diazonium ion. The mechanism of coupling reaction between phenoxide ions and diazotized amine is directed mainly to the *para* position, e.g.



Coupling reaction of aromatic amine and diazotized amine also occurs in the same way, e.g.

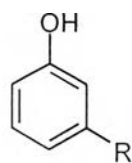


When the *para* position is already substituted, *ortho*-coupling occurs, but coupling reaction is never reacted at the *meta* position [12].

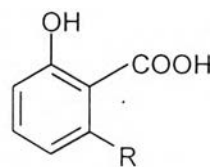
2.5 Cashew nut shell liquid

Cashew nut shell liquid (CNSL) is an oil obtained from the spongy layer between the inner and the outer shell of the cashew nut, *Anacardium occidentale*.

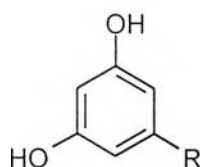
There are two processes to obtain cashew nut shell liquid from cashew nut, low temperature solvent extraction process and hot oil extraction process [13]. In the low temperature solvent extraction, the oil is almost completely phenolic in character, and the major components are anacardic acid (a mixture of 2-carboxy-3-alkylphenol), and cardol (a mixture of 5-alkylresorcinol). On the other hand, when using hot oil extraction process, most of the anacardic acid is decarboxylated, and two major components of the technical cashew nut shell liquid are the monophenol, cardanol (a mixture of 3-alkylphenol), and the resorcinol derivative, cardol, with a little of 2-methylcardol (a mixture of 2-methyl-5-alkylresorcinol) [14].



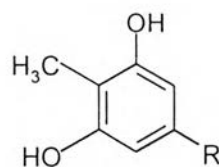
Cardanol



Anacardic acid



Cardol



2-methylcardol

R is $(\text{CH}_2)_{14}\text{CH}_3$

or $(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_5\text{CH}_3$

or $(\text{CH}_2)_7\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}(\text{CH}_2)_2\text{CH}_3$

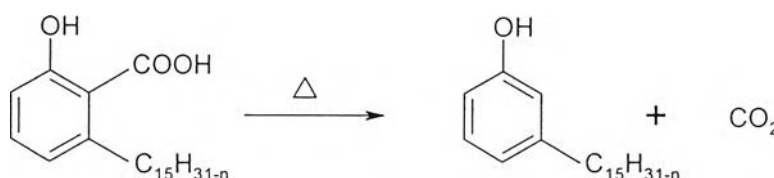
or $(\text{CH}_2)_7\text{CH}=\text{CHCH}_2\text{CH}=\text{CHCH}_2\text{CH}=\text{CH}_2$

CNSL is widely used in many industries. It has been used for manufacturing of brake lining and clutch facing. Other applications include cement and adhesives, laminated board manufacture, insulating varnishes, impregnating materials, modifier for phenol-based resin, indelible ink, plasticizers, germicides, and insecticides [15]. It has also been proposed to use it as a source of cardanol and anacardic acid for use as metal extractants [16].

2.6 Reactions in this research

2.6.1 Decarboxylation of CNSL

CNSL obtained from low temperature solvent extraction has two major components, anacardic acid and cardol. Anacardic acid is easily decarboxylated to cardanol, which is much stable component than anacardic acid. Anacardic acid was decarboxylated by heating at temperature of 110 °C for 3 hrs [13]. The reaction is outlined as follow:

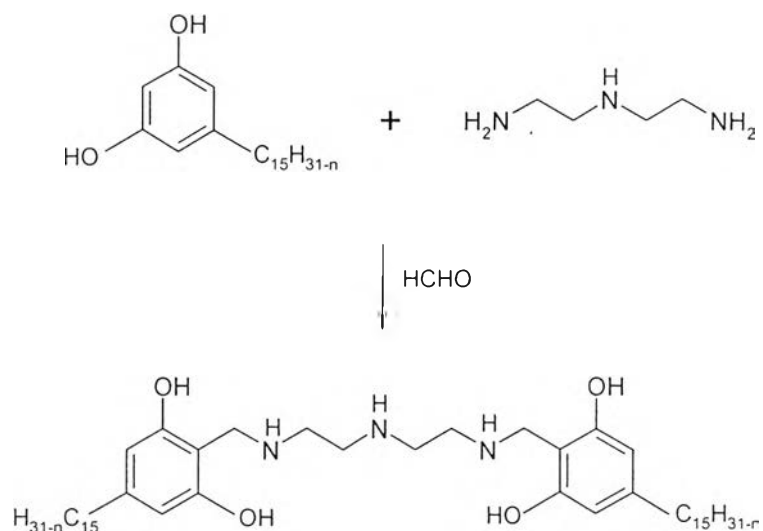


where $n = 0, 2, 4, 6$

2.6.2 Purification of cardanol

Decarboxylated CNSL contained mainly cardanol, cardol, and little of other phenols such as 2-methylcardol. Among these three components, cardol has the highest acidity, so that when reacting decarboxylated CNSL with the aldehyde and primary or secondary amine, cardol will react whilst leaving cardanol substantially unreacted. Thereby, cardanol can be removed from the reaction with high purity after working up.

The most preferred amine is diethylenetriamine (DETA), and it is preferred to carry out the reaction in a methanolic solution. The following reaction is postulated [15].

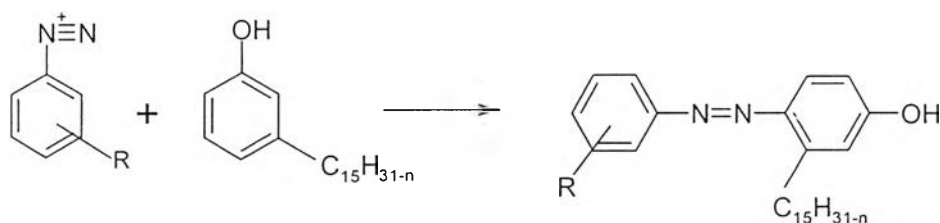


where $n = 0, 2, 4, 6$

The temperature of the reaction is usually ambient, since the reaction is slightly exothermic; some cooling is required in large batches.

2.6.3 Coupling reaction of cardanol and aniline derivatives

Marker dyes in this research are prepared by coupling reaction of diazotized aniline derivatives with 3-alkylphenoxide ions, which are derived from cardanol in an alkali solution. The reaction is schemed below.



where $n = 0, 2, 4, 6$

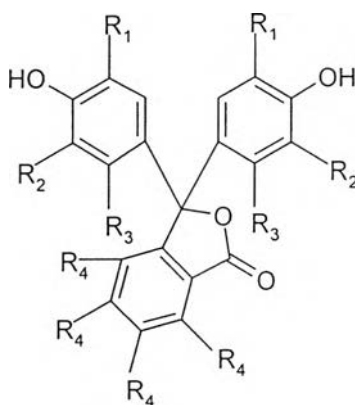
R = substituted groups such as nitro group, chloro group, etc.

2.7 Literature reviews

US Patent No. 6002056 “Colorless petroleum markers” [2]

Smith M.J., and Desai B., Dec. 14, 1999.

Petroleum products are marked with a marker, which is a derivative of isobenzofuranone.



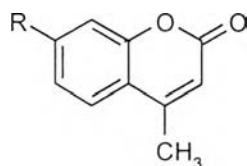
where R_1 is C_1 - C_8 alkyl or alkoxy group; R_2 and R_3 are hydrogen, alkyl group, alkoxy group, or part of naphthalene rings system; R_4 is any combination of bromine, chlorine, or hydrogen.

These marker compounds are synthesized by condensation of phthalic acid or its anhydride with 2-alkylphenol or 1-naphthol. Because these markers are colorless in petroleum products, their presence are detected by reacting them with a basic developing reagent such as an alkali metal hydroxide solution. The marker will undergo chromophoric reaction, and produces color in an extracted phase.

US Patent No. 5980593 "Silent fluorescent petroleum markers" [17]

Friswell, M.R., Zimin, A., and Caputo, P.A., Nov. 9, 1999.

The silent fluorescent markers have the general formula:



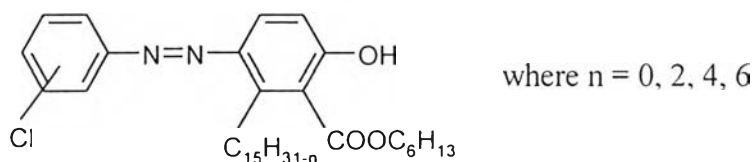
where R is selected from a linear or branched C_1 - C_{18} alkylcarboxy radical.

These compounds are synthesized from esterification reaction between an appropriate linear or branched C_1 - C_{18} alkylcarboxylic acid or acid halide, and 7-hydroxy-4-methylcoumarin. These markers are used for tagging petroleum products at levels of about 0.25 ppm to 100 ppm. They may be detected in the products by extraction with an alkali aqueous solution which produces strongly fluorescence when examine under ultraviolet light at wavelength of 365 nm.

Master thesis, Chulalongkorn university "Marker dyes from cashew nut shell extracted and chloroanilines" [3]

Thowongs, K., 1999.

Marker dyes, for gasoline and diesel fuel, are synthesized. These marker dyes have the formula:

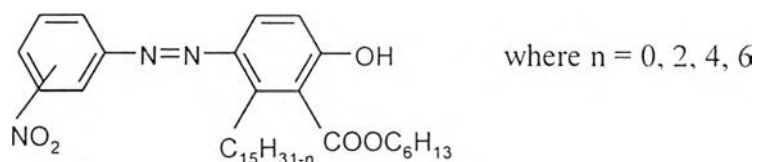


These marker dyes are synthesized by esterification reaction between cashew nut shell extracted and 1-hexanol. Then, the esterified products are coupled with chloroanilines to give yellow color marker dyes. These marker dyes are used for tagging gasoline and high-speed diesel at treat rate of 30 ppm, and can be detected by extraction the tagged fuel oils with 10% potassium hydroxide in methanol, these marker dyes will give yellow color in an extracted phase.

Master thesis, Chulalongkorn university “Marker dyes from cashew nut shell extracted and nitroanilines” [4]

Silapakampeerapab, S., 1999.

Petroleum fuel markers are synthesized. These marker dyes have the formula:

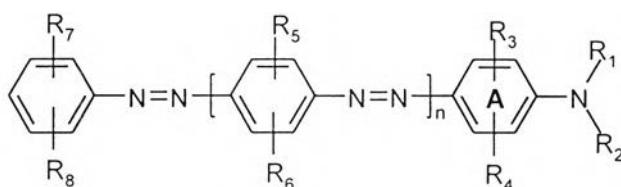


These marker dyes are synthesized by coupling reaction between esterified cashew nut shell extracted and nitroanilines. The esterified cashew nut shell extracted was obtained from esterification reaction between cashew nut shell extracted and 1-hexanol. These marker dyes can be used as marker dyes in gasoline and high-speed diesel at treat rate of 25 and 15 ppm, respectively. The detection of these markers in fuel oils is performed by extraction the dyed fuel oils with 2% potassium hydroxide in ethylene glycol, this will give clearly defined color in an extracted phase.

US Patent No. 5827332 "Azo dyes and a method of marking a hydrocarbon using an azo dye" [18]

Zeidler, G., Scholz, G., Krah, C., Beck, K.H., and Mayer, U., Oct. 27, 1998.

Azo dyes in this invention have the formula:



where the ring A may be benzofused,

n is 0 or 1,

R₁ is hydrogen or C₁-C₁₅ alkyl, which may be interrupted by from 1 to 4 ether oxygen atoms,

R₂ is C₁-C₁₅ alkyl, which may be interrupted by from 1 to 4 ether oxygen atoms,

R₃, R₄, R₅, R₆, and R₇ independently of one another are each hydrogen, C₁-C₁₅ alkyl, or C₁-C₁₅ alkoxy

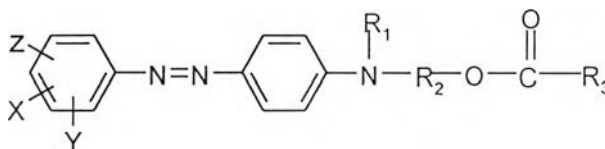
R₈ is hydrogen, C₁-C₁₅ alkyl, C₁-C₁₅ alkoxy, cyano, nitro, or a radical of the formula COOX₃, where X₃ is hydrogen, C₁-C₁₅ alkyl which may be interrupted by from 1 to 4 ether oxygen atoms.

These azo dyes can be used as pH-dependent markers for petroleum products, and under the action of aqueous alcoholic solution of a protic acid, in the presence or absence of zinc halide, aluminum halide or tin halide; these dyes will give a color reaction, i.e. a color change, accompanied by deeping of color.

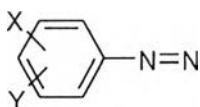
US Patent No. 5737871 "Method of preparing and utilizing petroleum fuel markers" [19]

Friswell, M.R., Apr. 14, 1998.

Petroleum markers known as "solid dispersed dye" are synthesized in a two-phase system. These markers have the formula:



where R_1 is C_1 - C_3 alkyl; R_2 is C_1 - C_3 alkylene; R_3 is C_1 - C_2 alkyl, preferably C_1 -alkyl; X and Y are selected from hydrogen, methyl, ethyl, methoxy, halogen, and nitro; Z is hydrogen or



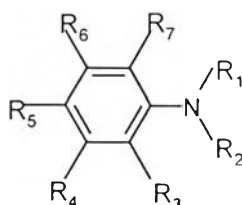
wherein X and Y are as defined above.

These dyes are synthesized in a two-phase system, including an acidic aqueous phase and a solvent phase. The dyes obtained can be used to tag petroleum products at levels of from about 0.25 to about 100 ppm. The markers are extracted from the tagged petroleum products with acidic aqueous solution, where the marker undergoes a chromophoric reaction, developing a strong color in the aqueous extraction solution.

US Patent No. 5627077 "Anilines as markers for mineral oils" [20]

Brenzinger, R.D., Raulfs, F.W., and Schlosser, U., May 6, 1997.

The formula of anilines:



where R_1 and R_2 are each hydrogen, unsubstituted or substituted alkyl, alkenyl or phenyl group

R_3 and R_7 are each hydrogen, unsubstituted or substituted alkyl, alkenyl, cyano, nitro, acyl, or acylamino group

R_4 is hydrogen, unsubstituted or substituted alkyl, alkenyl, hydroxy, amino, carboxyl, or sulfamoyl group

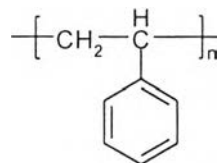
R_5 and R_6 are each hydrogen, unsubstituted or substituted alkyl, alkenyl, phenyl, nitro, acylamino, or carboxyl group.

These aniline derivatives are used for marking mineral oil. The anilines of the above-mentioned can be detected as markers in mineral oil by treating with an aqueous solution of the diazonium salt which is derived from an amine of the aminoanthraquinone, aminonaphthalene, aminothiophene, aminothiazole, or aminobenzoisothiazole series, and then coupled with a diazonium salt to form an azo dye.

US Patent No. 5512066 “Tagging materials for gasoline” [21]

Toman, J.J., and Biggs, W.R., Apr. 30, 1996.

Gasoline was tagged with polymer, such as polystyrene:

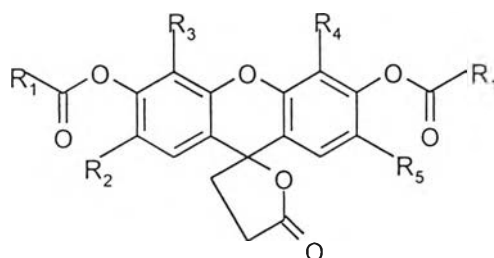


which have a number average molecular weight of at least 15,000. The tagged gasoline was detected by evaporating volatile hydrocarbon compositions at temperature of 122 °C and pressure of 5 mmHg to form a liquid residue. The molecular weight distribution of the residue was determined by gel permeation chromatography with evaporative light scattering as detector, but this technique may be interfered from the polymer additives, which was added in the fuel.

US Patent No. 5498808 “Fluorescent petroleum markers” [22]

Smith, M.J., Mar.12, 1996.

Colorless compounds, which developed fluorescence when extracted with an appropriate basic solution, for marking petroleum fuels are synthesized. These markers, which are the derivatives of Fluoroscein, have the general formula:



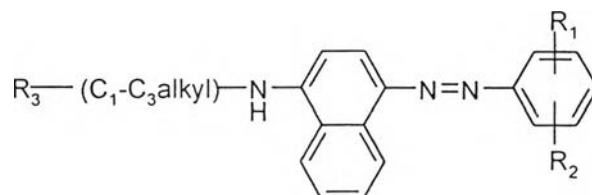
where R_1 is C_1 - C_{18} alkyl group or an aryl group; R_2 , R_3 , R_4 , and R_5 are hydrogen, chlorine, bromine, or C_1 - C_{12} alkyl group.

These markers are synthesized by converting Fluoroscein to an organic diesters to eliminate any tendency to partition into water. The diester may be derived from an organic acid, its anhydride or halide containing from one to eighteen carbon atoms. The ester markers can be added to any liquid petroleum products, and can be detected by reacting them with the developing reagent. Examples of the developing reagents are an aqueous solution of alkali metal hydroxide, and aqueous solution of the quaternary ammonium hydroxide. The base will hydrolyze the esters, and prompt formation of a highly fluorescent dianion, which may be variously colored.

US Patent No. 5490872 "Acid extractable petroleum fuel markers" [23]

Friswell, M.R., Hallissy, M.J., and Hinton M.P., Feb.13, 1996.

Petroleum fuels are tagged with markers having the formula:



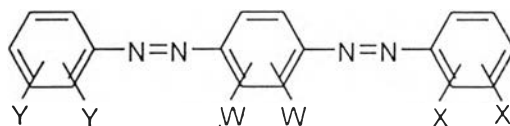
where R_1 and R_2 are selected from hydrogen, methyl, ethyl, methoxy, halogen, cyano, and nitro group; R_3 is selected from methyl, methoxy, methoxyethoxy, and morpholino group.

These markers are synthesized by azo coupling of an appropriate substituted aniline to an alpha-naphthylamine. They are generally colorless or have a pale yellow color in petroleum products. On the other hand, when extracted these tagged petroleum products with acidic aqueous solution, e.g., a 10% hydrochloric or formic acid solution, the variously colors are developed depending on R_1 , R_2 , and R_3 which are substituents in the molecule.

US Patent No. 5252106 "Base extractable petroleum markers" [24]

Halissy, M.J., Oct. 12, 1993.

Liquid petroleum products are marked with markers having the formula:



where W_s are selected from O-(C_1 - C_3 alkyl) and hydrogen, provided that at least one W_s is O-(C_1 - C_3 alkyl). X_s and Y_s are selected from hydrogen, alkyl, substituted alkyl, alkenyl, substituted alkenyl, aryl, substituted aryl, fused aryl, substituted fused aryl, halogen, nitro, cyano, and alkoxy group.

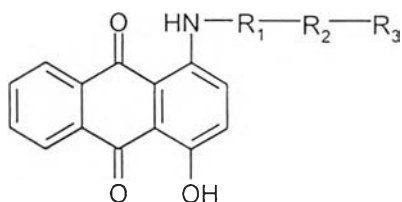
Markers of this invention are synthesized by azo coupling of an appropriate substituted aniline to a phenol, such as 2,6-di-*sec*-butyl phenol. Compounds of this formula are generally pale red, and at the end use level, e.g., 0.25-100 ppm, in petroleum product are not readily observable by naked eyes. These markers can be detected by extraction of the tagged products with an alkali

aqueous solution, e.g., 1-3% sodium hydroxide solution, the salt formed are generally deep blue color.

US Patent No. 5205840 "Markers for petroleum, method of tagging, and method of detection" [9]

Friswell, M.R., and Hinton, M.P., Apr. 27, 1993.

Liquid petroleum products are tagged with a marker, which is a compound or mixture of compounds having the formula:



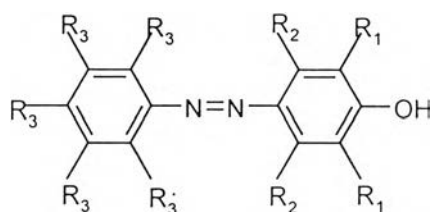
where R_1 is C_1 - C_6 alkyl, and R_2 and R_3 are nothing or O -(C_1 - C_3 alkyl).

These markers, which are known as "marker purple", are prepared by reaction of quinizarin, reduced quinizarin, or a mixture of quinizarin, and reduced quinizarin with the amine of formula, $H_2N-R_1R_2R_3$ wherein R_1 , R_2 , and R_3 are as defined above. These compounds have purple colors, but in the range from about 1-100 ppm, the marker imparts little visible color to the petroleum products. The marker may be detected in the petroleum products by extraction with a reagent comprising water, a strong base, and preferably a water-soluble oxygenated cosolvent or a water-soluble amine cosolvent. This reagent causes the markers to react and produce a clearly defined color that can use for identifying the petroleum products.

US Patent No. 5156653 "Silent markers for petroleum, method of tagging, and method of detection" [25]

Friswell, M.R., and Orelup, R.B., Oct. 20, 1992.

Liquid petroleum products are marked with markers having the formula:



Where R_1 and R_2 are each selected from hydrogen and C_1 - C_7 alkyl, provided that at least one R_1 is a C_3 - C_7 alkyl; and provided that R_3 are selected from hydrogen, nitro, halogen, cyano, and methyl, provided that at least one R_3 is selected from nitro, chloro, halogen, and cyano group.

These markers are synthesized by azo coupling of an appropriate substituted aniline to a 2,6-dibutyl phenol. The markers are detected in the tagged products by extraction the tagged fuel oils with a reagent comprising water, water-soluble amine, and a water-miscible cosolvent. The reagent reacts with the markers resulting in developing of the colors, that identifies the petroleum products.