CHAPTER I
INTRODUCTION

Nowadays, our country is extremely suffering from high-cost petroleum fuel problems because of the elevated cost of crude oil and the devalue of the currency. With the big gap between oil price in the country and outside the country, illegal oil smuggling is widespread. Therefore, Thai government loses a great amount of revenue. The illegal oil means untaxed clandestine or adulterated fuel oil by unscrupulous persons, by the mixing of lower grade products with premium grade products such as blending kerosene, stove oil or diesel fuel into regular grade gasoline or by adding regular grade gasoline to premium grade gasoline. To clamp down on widespread illegal oil trading, a marker system for fuel oil and other petroleum products has been necessary. Markers are used by the government to ensure that the appropriate tax has been paid on particular grades of fuel oil and petroleum products that are diluted or altered have been identified. It is generally used both visible and non-visible identification dyes to distinguish one grade product from another grade.

Marker systems have been used in many countries for a long time, but various drawbacks have existed. For example, furfural was widely used in European countries as a marker for fuel oil at concentration levels of 5-10 parts per million (ppm). But it was unstable to the extent that there was no positive identification after the usual storage period of three to six months. As another example, quinizarin and diphenylamine both were fairly sensitive marking materials, with simple detection procedures, but had shortcomings of poor solubility in fuel oil. This means that an undesirably large volume of them must be handled. Besides this, some radioactive materials were used as petroleum markers; but there was a restriction in some countries due to complicated apparatus, pollution, and safety reason. In Thailand, it has been an ordered to add markers into petroleum fuel, which are fluorescent markers, since December 1999. Because these markers were imported from a foreign country and their fluorescent properties, costly specific apparatus must be used in detection procedures. Therefore, it is important and desirable to have novel markers

for fuel oil that are oil-soluble dyes, detectable in a simple procedure even in very small amounts and capable of being rendered visible by a strong color reaction. Moreover, they could be synthesized through uncomplicated reactions with raw materials that are available and stable throughout a period of storage.

This research provides marker dyes for fuel oil that were synthesized from coupling reaction of imines and aniline diazonium salts of derivatives, e.g. *para*-nitroaniline, 2-chloro-4-nitroaniline, 4-chloro-2-nitroaniline, 2-methoxy-4-nitroaniline. Imine compounds were prepared from the reaction of salicylaldehyde and primary amines, e.g. ethylenediamine, diethylenetriamine, and triethylenetetramine. For a marking purpose, marker dye is typically added into fuel oil by about 5 ppm, within the detection limit as low as 0.5 ppm. The higher level of marker dye may be used so that it can be detected even when marked fuel oil is admixed with unmarked fuel oil. At such a low level, marker dyes are dissolved in fuel oil without imparting any color to the fuel oil or otherwise indicating their appearance to the naked eyes. To identify the marker dyes, marked fuel oil are extracted with oil-immiscible solution at suitable volume ratio of the extracted solution and fuel oil. These marker dyes could be quantified by measuring their absorption in the visible region. Various colors of the extracted marker dyes are dependent on the substituted groups of benzene ring.

The objectives of this research

The objectives of this research are to synthesize marker dyes for fuel oil from salicylaldehyde and amines, and to investigate their stability and presence of these marker dyes in fuel oil.

The scope of this research

This research is related to the synthesis of marker dyes from salicylaldehyde, aliphatic amine, and aromatic amines, which can be used at low levels in diesel oil with precisely quantitative determination. Moreover, they should be stable at least three months of storage. They should give clearly distinguish to the naked eyes when detected, and have no effects on the physical properties of marked diesel oil. The scope of this research is summarized as follows:

1. Synthesis of imine compounds from the reaction of salicylaldehyde and primary amines, e.g. ethylenediamine, diethylenetriamine, and triethylenetetramine.
2. Diazotization and coupling them with aniline derivatives, e.g. *para*-nitroaniline, 2-chloro-4-nitroaniline, 4-chloro-2-nitroaniline, and 2-methoxy-4-nitroaniline.
3. Characterization with FT-IR, MS and ^{1}H and ^{13}C-NMR spectroscopic techniques.
4. Detection of synthetic marker dyes after added into diesel oil both in field test and laboratory.
5. Determination of their quantities in marked diesel oil.
6. Study of the effects of synthetic marker dyes on physical properties of marked diesel oil.
7. Study of the stability after three months of storage.