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COLORED HYDROCARBONS

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9 Claims. (Cl. 44—59)

This invention relates to the art of coloring hydrocarbons such as petroleum distillates. It is particularly directed to the coloring of gasoline.

Gasolines, whether used for automobile engines, tractor engines or aviation engines, for example, are usually dyed a distinctive color such as yellow, orange, bronze, red, brown, blue, green and purple. Coloration is employed, for example, to identify the various grades of aviation gasoline, to distinguish manufacturers' brands, and in some cases to make adulteration or misuse difficult. For some applications there are specifications which regulate the composition and concentration of the dye or dyes used to color the gasoline. At the present time these specifications include Mil–F–5572 (military aviation gasoline), Mil–G–3056 (military motor gasoline), and ASTM D910–52T (civilian aviation gasoline). Further, the Surgeon General, U.S. Public Health Service, requires the coloring of gasoline that contains tetraethyl lead. Oil-soluble dyes are also frequently used to color other products such as furnace oils, lubricating oils, mineral oils, greases, waxes and synthetic lubricants.

Inasmuch as the most important use of the invention is in connection with the coloring of gasoline the invention will be described primarily with reference to the coloration of gasoline.

In coloring engine fuels such as gasoline it is very

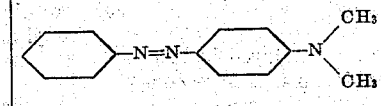
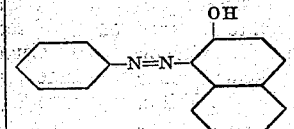
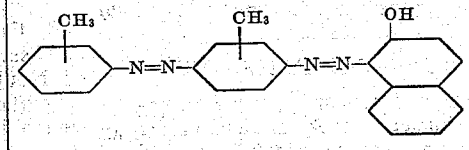
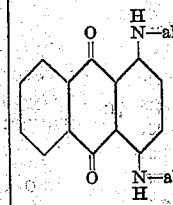
desirable that the coloring material have high tinctorial value inasmuch as the higher the tinctorial value of the coloring material the smaller the amount of coloring material required and the less the danger of excessive deposits of coloring material forming in the engine, e.g. in the intake system of the engine. Additionally, the coloring material should have adequate solubility in gasoline, should color the gasoline a satisfactory color and the colored gasoline should have satisfactory stability upon exposure to light and upon storage.

To be satisfactory for use in gasoline the coloring material or dye should:

(1) Have high tinctorial value.
(2) Be soluble in gasoline to the extent required for commercial use.
(3) Have adequate solubility in tetraethyl lead mixes if intended for coloring such fluids.
(4) Color gasoline to specified hues depending upon the application.
(5) Contain little or no material that is insoluble in gasoline.
(6) Be in a compact, noncaking, nondusting form.
(7) Have adequate color fastness in gasoline during storage or on exposure to light.
(8) Leave a minimum deposit in the motor induction system.
(9) Be compatible with other additives and should not affect the other properties of the fuel adversely.
(10) Be nonextractible from gasoline by water, caustic, or acid solutions.
(11) Meet the Surgeon General's requirement for minimum leaded gasoline color.

The current gasoline dyes are hydrocarbon-soluble, organic compounds, usually of the azo or anthraquinone type. Probably the four most commonly used are the yellow, orange, red and blue dyes prescribed in military and ASTM specifications for gasoline. These four dyes are:

TABLE I

Dye Color	Name	Structure	Specification Shade [1]
Yellow	N,N-Dimethyl-p-phenylazo aniline.		Aviation gasoline green; Motor gasoline red.
Orange	1-Phenylazo-2-naphthol		Aviation gasoline brown.
Red	Methyl derivatives of 1-(4-phenylazophenylazo)-2-naphthol.		Aviation gasoline red, blue, brown, purple; Motor gasoline red.
Blue	1,4-Bis(alkylamino)-anthraquinone.		Aviation gasoline red, blue, green, brown, purple.

[1] MIL–F–5572A; MIL–G–3056A; ASTM D910–537.

The specification shades of red (two), blue, green, brown, and purple are obtained by various mixtures of these dyes at certain specified concentrations.

I have discovered that

N-sec-butyl-p-(4-nitrophenylazo)aniline,
N-isobutyl-p-(4-nitrophenylazo)aniline,
N-n-butyl-p-(4-nitrophenylazo)amiline and
N-ethyl-p-(4-nitrophenylazo)-o-toluidine

are outstanding yellow dyes for hydrocarbon materials such as gasoline. These compounds are especially distinguished by their remarkable tinctorial power. As specifically shown hereinafter their tinctorial power for gasoline is more than three (in most cases more than four) times as great as that of N,N-dimethyl-p-phenylazoaniline, the dye most widely used to color gasoline yellow today. N-sec-butyl-p-(4-nitrophenylazo)aniline appears to be particularly advantageous and especial claim is made to this compound as a new compound and to its use for coloring hydrocarbons. The exceptional utility of the compounds of the present invention as dyes for gasoline, for example, could not have been predicted. By blending the yellow dyes of the present invention with other suitable dyes for gasoline colors, other than yellow, can be obtained.

In addition to having remarkable tinctorial power for gasoline the four azo compounds named in the preceding paragraph are otherwise satisfactory as dyes for gasoline. Thus, because of their great tinctorial power for gasoline and their relatively low cost of manufacture their use to color gasoline is considerably more economical than the standard yellow dye N,N-dimethyl-p-phenylazoaniline currently in large use. The savings in dyeing costs is apparent from the fact that only about one third to about one fourth as much dye is required as formerly. Further, because of the much smaller amount of dye required, there is much less danger of excessive amounts of dye depositing in the engine.

The azo dye compounds of the invention are prepared by coupling diazotized p-nitroaniline with N-secondarybutyl aniline, N-isobutyl aniline, N-n-butyl aniline and N-ethyl-o-toluidine, respectively. Advantageously the coupling reaction is carried out in the presence of a nonionic wetting agent and a large volume of water employing a slow crystallization technique. By carrying out the coupling reaction in the manner just indicated the dyes are obtained in an easily handled crystalline form rather than as a gummy material. When the dyes were prepared by carrying out the coupling reaction in a small volume and recovering the product formed by drowning in water, gummy products were obtained.

Nonionic wetting agents that can be employed include, for example, the alkylarylpolyether alcohols made by condensing alkylphenols with ethylene oxide in various proportions. Typical proportions range from six to fourteen parts of ethylene oxide by weight to one part alkyl phenol. Suitable alkylarylpolyether alcohol wetting agents include those sold under the trade names Triton X–102, Triton X–155, Sulfanole NO–9 and Tergitol NPX. Of the wetting agents used in preparing the azo dye compounds of the invention Triton X–102 is preferred.

TINCTORIAL STRENGTH AND HUE MATCH

Gasoline solutions of test and standard dyes were compared in a Duboscq colorimeter. Stock solutions of the dyes in benzene were prepared to contain 2.64 mg. of dye/cc. These stock solutions were pipetted into water-white, straight-run gasoline to obtain a dye concentration of 100 mg./gal. The dyed gasolines were then compared in the colorimeter at several different dial settings for the standard, corresponding to different liquid depths, by adjusting the test dye column to obtain the best intensity match. On the basis of several readings by two observers, the degree of hue match and the average tinctorial strength were determined. Tinctorial strength was calculated from the dial readings at matched color as follows:

$$\text{Tinctorial strength, percent} = \frac{\text{dial reading for std. dye}}{\text{dial reading for test dye}} \times 100$$

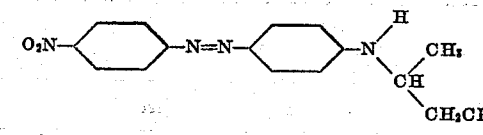
Thus, a tinctorial strength of 200% indicates that the experimental dye has twice the coloring power of the standard dye.

The reliability of this procedure using the colorimeter was checked by visual comparison of 8-ounce and ½-gallon samples of gasoline containing 10 mg. of standard dye per gallon and the tinctorial equivalent of the test dye. Reasonably good correlation was observed.

In the description which follows the preparation of the azo compounds of the invention and their use for coloring hydrocarbons, particularly gasoline, is described.

Example 1

13.8 parts of p-nitroaniline were added to a mixture of 19.3 parts of 95% sulfuric acid and 87 parts of water. The resulting mixture was warmed to complete solution of the p-nitroaniline and then poured, with stirring, into a mixture of 170 parts of ice and 10 parts of water. Then a solution of 7.1 parts of sodium nitrite in 15 parts of water were added immediately all at once. The reaction mixture thus obtained was stirred at 0° C.–5° C. for about 30 minutes to effect complete diazotization of the p-nitroaniline. The diazonium solution thus obtained was added slowly, with stirring, to a mixture of 14.9 parts of N-secondarybutyl aniline in 2 parts of an alkylarylpolyether alcohol and 2400 parts of water. The coupling reaction which takes place was carried out with stirring at a temperature of about 10° C.–15° C. until the reaction product crystallized (6 to 18 hours). The reaction mixture was then neutralized by the addition of 23 parts of sodium bicarbonate and stirred for 30 minutes longer. The precipitated dye compound was recovered by filtration and the dye recovered on the filter was washed with water until the washings were salt free. The dye compound thus obtained was dried at 40° C.–50° C. 29.7 parts of the brown dye N-sec-butyl-p-(4-nitrophenylazo)aniline having the formula:



were thus obtained. Upon recrystallization from isopropyl alcohol it melts at 100° C.–103° C.

Example 2

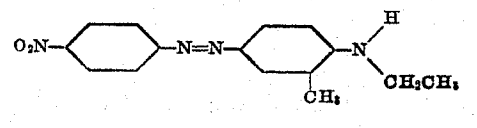
By the use of 14.9 parts of N-isobutyl aniline in place of N-secondarybutyl aniline in Example 1 a 56% yield of crude N-isobutyl-p-(4-nitrophenylazo)aniline is obtained, which, after recrystallization from methanol, had a melting point of 77° C.–84° C.

Example 3

By the use of 14.9 parts of N-n-butyl aniline in place of N-secondarybutyl aniline in Example 1 a good yield of N-n-butyl-p-(4-nitrophenylazo) aniline is obtained. A portion of this crude product recrystallized from ethanol had a melting point of 156° C.–158° C.

Example 4

By the use of 13.5 parts of N-ethyl-o-toluidine in place of N-secondarybutyl aniline in Example 1 a 46% yield of N-ethyl-p-(4-nitrophenylazo)-o-toluidine having the formula:



is obtained. This product had a melting point of 115° C.–120° C.

Example 5

Two dye solutions were prepared in water-white straight-run gasoline so as to contain 1.54 mg. of N-sec-butyl-p-(4-nitrophenylazo)aniline per gallon and 7.0 mg. of N,N-dimethyl-p-phenylazoaniline per gallon. The two solutions thus prepared looked identical in one-gallon quanities by visual observation under laboratory light. The results showed that N-sec-butyl-p-(4-nitrophenylazo) aniline is an excellent yellow dye for gasoline having a tinctorial strength of 455% and a good hue match.

Example 6

The colorimeter method described hereinbefore under the heading Tinctorial Strength and Hue Match was used to compare N-n-butyl-p-(4-nitrophenylazo)aniline with the standard yellow gasoline dye N,N-dimethyl-p-phenylazoaniline. The results showed that N-n-butyl-p-(4-nitrophenylazo)aniline is an excellent yellow dye for gasoline having a tinctorial strength of 476% and a good hue match.

Example 7

The colorimeter method described under Tinctorial Strength and Hue Match was used to compare the dye N-ethyl-p-(4-nitrophenylazo)-o-toluidine with the standard yellow gasoline dye N,N-dimethyl-p-phenylazoaniline. The results showed that N-ethyl-p-(4-nitrophenylazo)-o-toluidine is a very good yellow dye for gasoline having a tinctorial strength of 345% and an excellent hue match.

Example 8

The colorimeter method described above under the heading Tinctorial Strength and Hue Match was used to compare N-isobutyl-p-(4-nitrophenylazo)aniline with the standard yellow gasoline dye N,N-dimethyl-p-phenylazoaniline. The results showed that N-isobutyl-p-(4-nitrophenylazo)aniline is an excellent yellow dye for gasoline having a tinctorial strength of 400% and a good hue match.

Example 9

This example shows that the azo compounds of the invention are useful dyes for jet engine fuels and distillate burner fuels. Samples of a typical water-white straight-run jet fuel (JP–3 grade) were dyed with 10 mg./gal. of the standard yellow dye N,N-dimethyl-p-phenylazoaniline and 2.2 mg./gal. of the dye N-sec-butyl-p-(4-nitrophenylazo)aniline, respectively. 200 cc. samples of these dyed fuels looked identical when observed in eight-ounce oil sample bottles under laboratory light.

Example 10

N-n-butyl-p-(4-nitrophenylazo)aniline and the standard yellow dye N,N-dimethyl-p-phenylazoaniline were compared as dyes for the synthetic colorless lubricating oil di-(2-ethylhexyl) sebacate. The tests showed that 4.4 mg. of N-n-butyl-p-(4-nitrophenylazo)aniline colored the synthetic lubricating oil equally as well as 20 mg. of the yellow standard dye. A fairly good color match was obtained.

Other alkaline agents such as sodium acetate, sodium carbonate, disodium phosphate, potassium acetate and potassium carbonate can be used in place of sodium bicarbonate in Example 1.

Table II given hereinafter sets forth the results obtained when various azo compounds were compared with the standard yellow gasoline dye N,N-dimethyl-p-phenylazoaniline. The table sets forth the tinctorial strength, the hue match and the maximum solubility in grams per gallon of the dyes compared with the standard yellow gasoline dye.

DETERMINATION OF MAXIMUM SOLUBILITY IN GASOLINE

Straight-run gasoline in 200 cc. portions was mixed with dye on a slowly rotating wheel for 16 hours at 80° F. The saturated solutions were then allowed to stand at this temperature until the undissolved dye had completely settled. Then 50 cc. portions of the supernatant liquid were pipetted into weighed beakers of the type used for the gasoline gum test. The gasoline was evaporated in an ASTM gum unit at 210° F. under an air flow of 0.5 liter/second. After cooling and weighing the residue, and subtracting a blank for the undyed gasoline, the maximum solubility of the dye was calculated as grams per gallon.

TABLE II.—COMPARISON WITH STANDARD YELLOW GASOLINE DYE

Dye	Tinctorial Strength, Percent of Std.	Hue Match	Max. Solubility, g./Gal.[a]
N-methyl-p-(4-nitrophenylazo) aniline.	32	Good	6.8
N-ethyl-p-(4-nitrophenylazo) aniline.	73	Excellent	19.7
N-isopropyl-p-(4-nitrophenylazo)aniline.	161	Good	33.9
N-n-butyl-p-(4-nitrophenylazo)aniline.	476	do	8.9
N-isobutyl-p-(4-nitrophenylazo)aniline.	400	do	10.4
N-sec-butyl-p-(4-nitrophenylazo)aniline.	455	do	25.4
N-tert-butyl-p-(4-nitrophenylazo)aniline.	87	Fair	26.3
N-n-pentyl-p-(4-nitrophenylazo(aniline.	89	Good	
N-(1-methylhexyl)-p-(4-nitroazo)aniline.	189	do	35.2
N-cetyl-p-(4-nitrophenylazo) aniline.	43	Fair	
N-ethyl-p-(4-nitrophenylazo)-o-toluidine.	345	Excellent	5.1

[a]Solubility of yellow std.=35.4 g./gal.

The results set forth in Table II show that it could not have been predicted that

N-sec-butyl-p-(4-nitrophenylazo)aniline,
N-isobutyl-p-(4-nitrophenylazo)aniline,
N-n-butyl-p-(4-nitrophenylazo)aniline and
N-ethyl-p-(4-nitrophenylazo)-o-toluidine

would be outstanding yellow dyes for gasoline. No explanation for the poor tinctorial value of N-tert-butyl-p-(4-nitrophenylazo)aniline and N-n-pentyl-p-(4-nitrophenylazo)aniline is known.

It is here noted that the azo compounds of the present invention in addition to having outstanding tinctorial power for gasoline meet the other requirements of a satisfactory gasoline dye such as oil solubility, distinctive shade, color fastness, and compatibility with other additives such as tetraethyl lead fluid, antioxidants and metal deactivators. The properties of a satisfactory gasoline dye have been set forth more fully hereinbefore and the azo compounds of the invention satisfactorily meet the properties previously set forth.

No particular techniques are required to get the azo dyes of the present invention dissolved in gasoline. They are handled and added to gasoline by the same processes now used for other powdered gasoline dyes. Perhaps the most common method now in use is the "dry dye eductor" system wherein powdered dye is sucked directly from the shipping container into the gasoline being dyed using standard equipment and controls to insure proper dosage. Inasmuch as the manner in which the dyes would be dissolved in gasoline is well known to those skilled in the art to which this invention is directed, no further discussion on this point is believed necessary.

I claim:

1. A petroleum distillate colored with a dye compound selected from the dye compounds consisting of

N-sec-butyl-p-(4-nitrophenylazo)aniline,
N-isobutyl-p-(4-nitrophenylazo)aniline,
N-n-butyl-p-(4-nitrophenylazo)aniline and
N-ethyl-p-(4-nitrophenylazo(-o-toluidine

dissolved therein, said dye compound being present in the proportion of about 1.50 mg. to about 100 mg. per gallon of said petroleum distillate.

2. A gasoline colored with a dye compound selected from the dye compounds consisting of

N-sec-butyl-p-(4-nitrophenylazo)aniline,
N-isobutyl-p-(4-nitrophenylazo)aniline,
N-n-butyl-p-(4-nitrophenylazo)aniline and
N-ethyl-p-(4-nitrophenylazo)aniline

dissolved therein, said dye compound being present in the proportion of about 1.50 mg. to about 100 mg. per gallon of said gasoline.

3. A gasoline containing tetraethyl lead colored with a dye compound selected from the dye compounds consisting of

N-sec-butyl-p-(4-nitrophenylazo)aniline,
N-isobutyl-p-(4-nitrophenylazo)aniline,
N-n-butyl-p-(4-nitrophenylazo)aniline and
N-ethyl-p-(4-nitrophenylazo)-o-toluidine

dissolved therein, said dye compound being present in the proportion of about 1.50 mg. to about 100 mg. per gallon of said gasoline.

4. A petroleum distillate colored with N-sec-butyl-p-(4-nitrophenylazo)aniline dissolved therein, said N-sec-butyl-p-(4-nitrophenylazo)aniline being present in the proportion of about 1.50 mg. to about 100 mg. per gallon of said petroleum distillate.

5. A gasoline colored with N-sec-butyl-p-(4-nitrophenylazo)aniline dissolved therein, said N-sec-butyl-p-(4-nitrophenylazo)aniline being present in the proportion of about 1.50 mg. to about 100 mg. per gallon of said gasoline.

6. A gasoline containing tetraethyl lead colored with N-sec-butyl-p-(4-nitrophenylazo)aniline dissolved therein, said N-sec-butyl-p-(4-nitrophenylazo)aniline being present in the proportion of about 1.50 mg. to about 100 mg. per gallon of said gasoline.

7. A gasoline colored with N-isobutyl-p-(4-nitrophenylazo)aniline dissolved therein, said N-isobutyl-p-(4-nitrophenylazo)aniline being present in the proportion of about 1.50 mg. to about 100 mg. per gallon of said gasoline.

8. A gasoline colored with N-n-butyl-p-(4-nitrophenylazo)aniline dissolved therein, said N-n-butyl-p-(4-nitrophenylazo)aniline being present in the proportion of about 1.50 mg. to about 100 mg. per gallon of said gasoline.

9. A gasoline colored with N-ethyl-p-(4-nitrophenylazo)-o-toluidine dissolved therein, said N-ethyl-p-(4-nitrophenylazo)-o-toluidine being present in the proportion of about 1.50 mg to about 100 mg. per gallon of said gasoline.

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