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FUEL TREATING AGENT

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This invention relates to improvements in the coloring of petroleum products, particularly relatively colorless petroleum products used as fuels.

The use of coloring materials in petroleum products, particularly gasoline, has become widespread and is designed to serve a number of purposes such as distinguishing grades of fuels, identifying origins of fuels, marking the presence of lead in the fuel and in some jurisdictions to indicate tax-free material. Colors are added either directly or in combination with gasoline treating fluids, such as tetraethyl lead or the like, and varied problems of solubility, precipitation and color strength are thereby presented.

Various methods of introducing dyes into petroleum products have been devised, but none is completely satisfactory and many common oil soluble dyes have been restricted in their application to coloring fuels because of low solubility or other difficulties.

One commonly used method of introducing dyes into petroleum fuels has been to resort to an intermediate solvent such as benzol. This has proved generally not satisfactory as most desired dyes are not highly soluble in benzol and large amounts of benzol must be used.

A second method has been to mix the dye with a diluent prior to addition to the petroleum itself. In this connection it is seen that if color of the fuel is to serve as a distinguishing mark for grade or tax purposes or to show the presence of added treating material, somewhat precise standardization will be necessary to insure the reproduction of the standard color desired. It is therefore desirable that the diluent should be a solid as the mixture of powdered dye and diluent can be handled and shipped without danger of the two constituents separating and destroying the standardization. The paste or liquid which results from a solid dye and a liquid diluent tends to separate, whereby the precise standard of color required is not maintained. The diluent should have no deleterious effects upon the fuel or applications thereof and it is of course necessary that the diluent be soluble in the fuel.

Heretofore the few solid products generally used for diluents have not been free of these disadvantages. Some diluents, while inert chemically, have the bad feature of subliming from the dye during storage, coating the tops and sides of the storage container, changing the relationship of dye and standardizer, and thus the

color in the ultimate fuel. Other diluents, while of non-subliming character, have disadvantageous effects upon the fuel in that they add acidic materials, accelerate gum formation in the fuel and particularly where leaded fuels are used, tend to remove the lead from its proper field of activity, forming the lead salt of the acidic material.

A third method of coloring fuels has been to add the dye directly in the proper amount to a given amount of fuel and where this is possible it is of course more desirable than the above noted procedures. However, for the most part storage tanks and tank cars are not equipped with mixing apparatus which will permit the homogeneous blending of the dye and the fuel so that ordinarily this method of procedure is impractical.

The problem of producing a standard color in fuels is further complicated by the fact that most desirable dyes are not completely soluble in the fuels themselves or in lead or other treating fluids, so that the use of the requisite amount to produce the desired color either with or without solution aids often results in a residue of undissolved dye which has a deleterious effect upon the fuel or treating agent and destroys the standard color.

I have now discovered that a class of compounds containing as their characteristic structural feature, two phenyl groups, either joined directly or by a substituent, which does not produce water soluble or acidic compounds possess the singular property of increasing the rate of solution of dyes in the treated or untreated fuel to a marked extent, so that the dyes may be used in the proper concentration without the use of an intermediate solvent and without leaving a residue of undissolved dye in the fuel. Of these compounds I have found useful those members of the group which are directly joined, such as diphenyl and its substituted derivatives, such as alkyl or halogen derivatives, particularly the chlorine derivative or those derivatives which are joined by substituents having no chemical characteristics incompatible with the properties of diphenyl itself. I have found preferable diphenyl itself.

By using diphenyl I may add the mixture of dye and diphenyl directly to the fuel and the same will diffuse through the body of the fuel in a short time without the necessity of providing special blending and mixing means.

I have also discovered that diphenyl and its derivatives are particularly useful in aiding the

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solution of dye in a small amount of gasoline treating fluid, such as commercial ethyl fluid, tetraethyl lead, ethylene dibromides and chlorides or the like and that no interference exists between the diphenyl compound and the treating fluid either before or after the addition of the mixture to the fuel itself.

Diphenyl has the advantage of being a solid material melting at about 51° C. to 52° C. and is itself soluble in petroleum products such as gasoline and the like. It furthermore adds no deleterious or undesired components to fuels such as gasoline, and being stable, solid and substantially non-sublimable, permits accurate standardization. Concentrations as low as 10% of diphenyl in the dye may be used effectively and higher concentrations have been found to cause no deleterious effect upon the fuel. Since the use of diphenyl results in increased velocity of solution of the dye in the fuel, whereby no residual undissolved material remains in the fuel mixture, increased color strength may often be obtained with less dye than heretofore used with other standardizing agents.

All types of oil soluble dyes which will dissolve in fuels have been found to be benefited by this treatment; anthraquinone dyes are found to be particularly advantageously affected. These compounds include phenylated amino anthraquinones, oxyphenyl amino or amino anthraquinone, all compounds of anthraquinone containing either amino or hydroxy groups, the diaryl amino anthraquinones being particularly advantageously affected.

For example, when 1-4 ditoluido-anthraquinone is mixed with 15% diphenyl and the mixture blended with gasoline, an increase in color strength of from 4% to 5% occurs. The dye and diphenyl dissolve completely and permanently in the fuel. It will be understood that dyes are commonly used in fuels in the approximate proportions of from two or three to sixteen or twenty ounces of dye in 10,000 gallons of gasoline (70,000 lbs. approximately). I have found it useful to employ quantities of diphenyl ranging from 10 to 75% of the total of material added to the fuel but quantities above and below these limits have been found to have advantageous effects upon the solubility of the dye and the fuel. Equally good results are obtained by mixing the dye with the diphenyl by grinding the two together or by making a melt with the dyestuff and then grinding.

Other dye-diphenyl combinations which have been found to be useful are as follows:

1. 80 parts of 1-4 ditoluido anthraquinone and 20 parts of diphenyl.

2. 70 parts of 1-oxy 4-para toluido-anthraquinone and 30 parts of diphenyl.

3. 50 parts of 1-2 dihydroxy anthraquinone (alizarine) and 50 parts of diphenyl.

4. 50 parts of 1-4 dihydroxy anthraquinone (leuco chinizarine) and 50 parts of diphenyl.

5. The azo dyestuff formed by coupling 70 parts of ortho anisidine and beta naphthol, and 30 parts of diphenyl.

6. 60 parts of 1-methylamino 4-para toluido anthraquinone and 40 parts of diphenyl.

Examples of other dyes commonly used in coloring gasoline to which this invention may be applied are the amino anthraquinones, 1-5 ditoluido anthraquinone, 1 amino 2-4 ditoluido anthraquinone, 1-4 amido anthraquinone, 1 methyl amido 4 methyl amido anthraquinone, 1 amido 4 hydroxy anthraquinone, 1-4 dianilido anthra-

quinone, 1-oxy 4 para anilido anthraquinone, 1-5 dianilido anthraquinone, 1 amino 2-4 dianilido anthraquinone. Other dyes also useful for this purpose are amino azobenzol azo betanaphthol, xyldine azo beta naphthylamine, aniline azo dimethyl aniline, and ortho chlor aniline azo phenyl betanaphthylamine.

In the case of treated fuels, particularly gasolines treated with commercial ethyl fluid which comprises roughly two-thirds tetraethyl lead and one-third ethylene dibromide and dichloride, a special situation exists in that only a small percentage of dye, such as 5%, is soluble in ethyl fluids in any event. The amount which dissolves while sufficient to identify the ethyl fluid is not enough to render the color of the gasoline sufficiently distinctive to comply with various statutory requirements respecting gasoline containing lead and accordingly it is necessary to add further dye-diphenyl composition to the gasoline after the ethyl fluid saturated with dye-diphenyl combination is added. The following examples will serve to illustrate this:

7. From .5 gm. to 1 gm. of a mixture of 1 gm. of diphenyl and 3 gm. of 1-4 ditoluido anthraquinone is combined with 28 cc. of ethyl fluid of the approximate composition above set forth. This quantity of ethyl fluid is sufficient to treat about 400 gallons of aviation gasoline. The ethyl fluid dye-diphenyl composition may be added to this quantity of gasoline, the remainder of the dye-diphenyl composition being added to the gasoline subsequently. A considerably larger quantity of ordinary gasoline may be treated with this quantity of ethyl fluid and the concentration of the dye adjusted if desired.

8. In the same manner .5 gm. to 1 gm. of a mixture of 1 gm. of diphenyl and 3 gm. of 1 oxy 4 para toluido anthraquinone may be combined with the same amount of ethyl fluid which is thereupon added to the same amount of gasoline as stated in Example 5 and the remainder of the dye-diphenyl composition added thereafter.

If desired all of the dye-diphenyl composition may be added to the fuel before or after addition of ethyl fluid thereto, but it is desirable to add as much dye as possible to the ethyl fluid before it is added to the gasoline, in order that the poisonous nature of the ethyl fluid may be clearly marked.

In both of the examples the color produced is of sufficient depth to identify both the ethyl fluid and the fuel plainly and is moreover permanent and non-precipitating.

Numerous other applications of this invention are possible; for example, any dye actually soluble in petroleum products may be used with diphenyl with a consequent increase in effective color strength, but of course the greatest benefit of the invention is apparent when the diphenyl is applied to difficultly soluble dyestuffs. Furthermore the more difficultly soluble dyes are added more in proportion by the use of diphenyl and their velocity of solution in fuels is increased considerably more than in the case of the more soluble types of dyes. Examples of dyes which receive maximum benefit are the 1-4 ditoluido anthraquinone, 1 methyl amino 4 toluido anthraquinone and the 1-oxy 4-para toluido anthraquinone.

Diphenyl compounds appear to have the effect of placing more solid dyestuff in the liquid phase in a two-phase system. It is believed that solutions of large molecule dyes such as are commonly used in petroleum products are not en-

tirely true solutions, but comprise two-phase systems, consisting of the solid dyestuff and the dyestuff dissolved in liquid petroleum. Diphenyl appears to have the effect of permitting more solid undissolved dye to be present in a liquid phase which results in an increase in color strength. Thus the tendency of diphenyl in the fuel is to produce a high degree of supersaturation of dye therein.

I claim:

1. A composition of matter for coloring petroleum products comprising a combination of diphenyl with a dyestuff suitable for coloring petroleum products.

2. A composition of matter for coloring petroleum products comprising the combination of diphenyl with an oil soluble dye.

3. A composition of matter for coloring petroleum products comprising diphenyl and an anthraquinone dye.

4. A composition of matter for coloring petroleum products comprising diphenyl and an amino or substituted amino anthraquinone dye.

5. A composition of matter for coloring petroleum products comprising diphenyl and 1-4 ditoluido anthraquinone.

6. A composition of matter for coloring pe-

troleum products comprising diphenyl and 1-oxy 4-para toluido anthraquinone dye.

7. A composition of matter for treating petroleum products comprising ethyl fluid, diphenyl and a petroleum soluble dye.

8. A composition of matter for treating petroleum products comprising tetraethyl lead, ethylene dibromide, and dichloride, diphenyl, and a dye.

9. A composition of matter for treating petroleum products comprising tetraethyl lead, ethylene dibromide and dichloride, diphenyl, and an anthraquinone dye.

10. A composition of matter for treating petroleum products comprising tetraethyl lead, ethylene dibromide and dichloride, diphenyl and an amino or substituted amino anthraquinone dye.

11. A composition of matter for treating petroleum products comprising tetraethyl lead, ethylene dibromide and dichloride, diphenyl and 1-4 ditoluido anthraquinone.

12. A composition of matter for treating petroleum products comprising tetraethyl lead, ethylene dibromide and dichloride, diphenyl and 1-oxy 4-para toluido anthraquinone.

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