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STABILIZING SOLUTION OF TETRA-ALKYL LEAD COMPOUNDS

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This invention relates to stabilizing solutions of tetra-alkyl lead compounds; and it comprises a method of stabilizing said solutions particularly ethyl gasoline wherein the development of a hazy appearance is inhibited by adding to such solutions small quantities of cinnamylidene aniline; all as more fully hereinafter set forth and as claimed.

This application is a division of our copending application, Serial No. 316,686, as filed January 31, 1940.

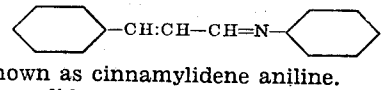
It is customary in the production of so-called "ethyl gasoline" to add to a good grade of gasoline a small amount of a tetra-alkyl lead compound, usually tetra-ethyl lead to reduce the tendency of the gasoline to cause knocking in high compression gasoline engines. The amount of tetra-alkyl lead compound added to a gasoline depends upon the nature of the gasoline and the desired anti-knock rating. Tetra-ethyl lead is customarily added to the gasoline in the form of a concentrate called "ethyl fluid" which is a solution containing a mixture of tetra-ethyl lead, alkyl di-halide (e. g., ethyl di-bromide or ethyl di-chloride or both) and a small amount of a dye to impart a distinctive color to the gasoline. The function of the alkyl di-halide is to limit the formation of lead oxide from tetra-alkyl lead in the cylinders of the engine by forming volatile halides of lead which are carried out in the exhaust. The ethyl fluid is added to the gasoline in a quantity sufficient to produce the desired anti-knock rating and in some cases a relatively small amount may be required, while, in other cases, for example, in the preparation of certain aviation grades of gasoline, a relatively large amount may be added. Gasoline to which a large amount of tetra-ethyl or other tetra-alkyl lead has been added is often referred to as a "heavily leaded" gasoline.

Although tetra-alkyl lead compounds, and, in particular tetra-ethyl lead, are particularly efficient for imparting anti-knock properties to gasoline, their employment is not entirely free from disadvantage. For one thing, leaded gasoline tends to develop a hazy appearance upon standing, particularly in the presence of strong sunlight. For example, in direct sunlight in the summer time, ethyl gasoline may develop a perceptible haziness after an hour or two of exposure, and longer periods of exposure result in a very marked haziness and precipitation occurs. This phenomenon is also sometimes observed in the ethyl fluid itself.

The formation of haze in gasoline is objectionable because the gasoline is not as marketable as a clear product; customers prefer a product which is crystal clear. A further and perhaps more important objection is that a reduction in the octane rating of gasoline is frequently associated with haze formation. Also damage is likely to occur in the fuel lines and carburetor. The development of haze in ethyl fluid itself is also objectionable, because when a hazy ethyl fluid is blended with gasoline to form ethyl gasoline, the haze is introduced into the fuel with all its attendant disadvantages.

An object achieved by this invention is to provide solutions of tetra-alkyl lead compounds, such as ethyl fluid and ethyl gasoline which are stabilized against haze formation.

We have found that haze formation in solutions of tetra-alkyl lead compounds, such as ethyl fluid and ethyl gasoline, can be very materially reduced by incorporating in such solution small quantities, proportioned on the amount of tetra-alkyl lead compound in solution, of a compound having the formula



and known as cinnamylidene aniline.

Cinnamylidene aniline may be added with advantage to solutions generally of tetra-alkyl lead compounds and more particularly to all types of leaded gasoline. The manner of incorporating the cinnamylidene aniline in solution of tetra-alkyl lead compounds is not critical. It may be incorporated in the ethyl fluid at any stage during the preparation thereof, or it may be incorporated in the gasoline prior to the addition of ethyl fluid, along with the ethyl fluid, or subsequent to blending the ethyl fluid with the gasoline.

Even very small amounts of cinnamylidene aniline are sufficient to exert a substantial stabilizing effect against light in fluids containing tetra-alkyl lead compounds. In general with higher percentages of tetra-alkyl lead compounds, higher amounts of cinnamylidene aniline are required. Within the range of about 0.01 to about 1 per cent by weight of tetra-ethyl lead in solution, a substantial stabilizing effect is exerted by from about 3 to about 120 pounds of cinnamylidene aniline per thousand barrels of gasoline. Within the range from about 0.02 to about 0.40 per cent by weight of tetra-ethyl lead in solution, which represents a commercial range, it is advantageous to employ from about 5 to about 20 pounds of cinnamylidene aniline

per thousand barrels of gasoline. Such amounts will exert a marked stabilizing effect against light and will produce a commercial ethyl gasoline which is satisfactorily stable to light under the usual conditions of exposure.

The application of cinnamylidene aniline to the stabilization of solutions of tetra-alkyl lead compounds against haze formation is not limited to leaded gasoline and it may be incorporated directly in the ethyl fluid with advantage. When cinnamylidene aniline is incorporated in the tetra-alkyl lead concentrate, it stabilizes the concentrate during storage and shipment, and the stabilized concentrate containing the cinnamylidene aniline can then be added to gasoline to impart thereto both anti-knock properties and resistance to haze formation. In such case the amount of cinnamylidene aniline incorporated in the ethyl fluid is generally somewhat greater than is required for stabilization of the concentrate so that by the addition of the usual small amount of ethyl fluid to the gasoline a suitable stabilizing amount of cinnamylidene aniline will be incorporated in the gasoline. Generally from 1 to 10 per cent by weight, based on the tetra-ethyl lead, of cinnamylidene aniline very satisfactorily stabilizes commercial tetra-ethyl lead concentrates, such as ethyl fluid and on adding the stabilized concentrate to gasoline to produce ethyl gasoline, a satisfactorily stabilized ethyl gasoline is obtained.

The cinnamylidene aniline of our invention in addition to its stabilizing properties has other properties which particudarly recommend it for this use. It does not adversely affect the oxygen stability of the gasoline. Samples of cracked ethyl gasoline containing cinnamylidene aniline have been aged and tested for oxygen stability and by the copper dish method for gum formation. The presence of the cinnamylidene aniline did not promote either oxygen instability or gum formation. It is non-corrosive to common packaging materials such as steel, zinc, copper and tin and is compatible with the dyes commonly used in ethyl gasoline to give it a distinctive appearance. It is sufficiently soluble in gasoline to accomplish the intended stabilization. Furthermore it is insoluble in water, which is a distinct advantage because contact with water will not result in leaching the stabilizer out of the gasoline. Continued storage of gasoline containing cinnamylidene aniline does not affect its stabilizing properties. Also cinnamylidene aniline can be readily prepared from compounds available on the market at a relatively low cost, and its mode of preparation is simple and inexpensive.

The following specific example will serve to illustrate the excellent haze inhibiting properties of cinnamylidene aniline.

Example I.—Ethyl gasoline containing 0.1 per cent by weight of tetra-ethyl lead (added in the form of ethyl fluid comprising tetra-ethyl lead, ethylene dibromide and a dye) was treated with cinnamylidene aniline in the proportion of 20 pounds of the latter per thousand barrels of gasoline, the resulting solution was exposed for 5 hours to sunlight and the appearance of the gasoline was noted. At the end of 5 hours exposure there was a small degree of haziness but a great improvement over the appearance of the same gasoline containing no cinnamylidene aniline. This was considered a fair stabilization.

While our invention has been described herein with reference to certain specific embodiments and spcific examples thereof, we do not intend that our invention shall be limited to such embodiments and examples except as hereinafter defined in the appended claims.

What we claim is:

1. A method of producing a light-stable solution of a tetra-alkyl lead compound, which comprises incorporating in said solution cinnamylidene aniline in amount sufficient to inhibit the formation of haze in said solution.

2. The method of claim 1 wherein the tetra-alkyl lead compound is tetra-ethyl lead.

3. A method of producing a light-stable anti-knock motor fuel containing a tetra-alkyl lead compound, which comprises incorporating in said motor fuel cinnamylidene aniline in amount corresponding to 0.01 to 1.0 per cent by weight of the tetra-alkyl lead compound.

4. As an improved anti-knock motor fuel stable to light, a gasoline containing 0.02 to 0.4 per cent by weight of tetra-ethyl lead and about 5 to 20 pounds of cinnamylidene aniline per thousand barrels of gasoline.

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