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MOTOR FUEL

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This invention relates to improvements in motor fuels, more particularly to improved blends of alcohol and hydrocarbon oil fractions for use in internal combustion engines.

As is known, ethyl alcohol, which is to be employed in a motor fuel, according to law must be denatured. The denaturation of ethyl alcohol intended for this use presents special problems which are not necessarily encountered in the denaturation of other forms of industrial alcohol. In the denaturation of power alcohol, like other industrial alcohol, it is desirable that the denaturant should have a boiling point or boiling range quite close to that of ethyl alcohol so that separation of the two by the expedients of fractional distillation is rendered difficult. Similarly, like the typical industrial alcohol denaturants, the power alcohol denaturant should be of such a character that, when employed even in small amounts, it should be decidedly distasteful and preferably nauseating. Again, like typical denaturants, the power alcohol denaturant preferably should be of such high volatility that, when dissolved in alcohol, its presence, even in small quantities, should be unmistakably apparent.

In addition to these requirements, other special criteria of effectiveness apply to power alcohol denaturants. The power alcohol denaturant should be of such a character that it does not either mediately or immediately disadvantageously combine, or react with the gasoline to produce undesirable substances, such as gums, colored compounds, and the like. Again, the power alcohol denaturant should be of such a character that it does not tend to induce or accelerate corrosion of the metal parts of the engine in which it is employed.

While many suggestions have been proposed in the past for denaturing alcohol, these were concerned largely with typical industrial alcohol intended for employment as a solvent and the like, in which the special problems mentioned hereinbefore did not obtain.

The present application relates to a method of denaturing power alcohol, and to special alcohol denaturants which are peculiarly efficacious in that they serve not only to denature the alcohol, per se, but serve to produce a denatured alcohol which is blendable with gasoline and which, after blending, subserves a number of additional beneficial functions in the ultimate blend.

According to the present invention, blends of gasoline and denatured alcohol are produced in which the ultimate fuel contains substances which not only effectively denature the alcoholic content, but which act as negative oxidation catalysts to inhibit gum formation in the gasoline, and which furthermore functions as blending agents. As will be seen more fully hereinafter, the denaturant concentrate which is employed is of a special character, comprising in itself a blend or solution of certain substances which have a multiple function in the ultimate composition.

Briefly considered, the invention comprehends the concept of effectively denaturing power alcohol, intended for blending with gasoline oil fractions, by adding thereto effective amounts of crude methanol. The crude methanol contemplated herein comprises a distillate from a neutralized pyroligneous acid which contains, in addition to methyl alcohol itself, certain other bodies, such as higher alcohols of the type of allyl alcohol, acetone, and phenolic bodies, which latter constitute, at the one time, effective denaturants and blending agents, and reducing agents or gum inhibitors.

The crude wood methanol employable under the present invention may also comprise a distillate, of any given cut, produced from the neutralized pyroligneous acid in combination or blended with certain selected fractions produced by the steam distillation of the wood tar. In this manner, the respective proportions of denatured alcohol and ketonic bodies, on the one hand, and of the combined denaturing and gum inhibiting and blending agents, on the other, may readily be controlled. In brief then, the invention comprehends the concept of producing a power alcohol which is denatured with cheap, readily available substances which perform multiple and advantageous functions in the ultimate product.

As is known in the process of producing methanol by destructive distillation of hard wood, the wood is heated in a closed retort and the volatile products are separated into two fractions, namely, the non-condensable gases and the crude (tar-containing) pyroligneous acid. The tar is allowed to settle out of the acid and the acid is then distilled. Such distillation serves to separate the relatively volatile constituents from the residual tarry or relatively non-volatile products.

This crude pyroligneous acid is an aqueous solution comprised of a very complex mixture containing upward of thirty-five or more distinct compounds. Included in the pyroligneous acid are such compounds as the fatty acids, methyl alcohol, allyl alcohol; aliphatic aldehydes, such as acetaldehyde, furfural and methyl furfural; esters such as methyl formate and methyl acetate; ketonic bodies such as acetone, methyl ethyl

ketone, ethyl propyl ketone, and the like; heterocyclic compounds such as valero-lactone and pyridine; and phenolic bodies such as pyrocatechin.

In the refining of this pyroligneous acid, for the purpose of producing methyl alcohol, several distillations are performed. After the initial distillation, the substantially tar-free aqueous pyroligneous acid is generally neutralized with lime to throw down and recover the acetic acid as acetate of lime. The neutralized pyroligneous acid is then distilled again and the distillate comprises the volatile constituents of the acid liquor. This distillate consists mainly of water, methyl alcohol, acetone, methyl acetate, allyl alcohol and a number of other complex substances such as phenolic bodies. These phenolic bodies are more soluble in the methyl alcohol than in the water. In the usual final stages of rectification of pyroligneous acid, this solubility is utilized to separate out such substances. According to the present invention, as noted hereinbefore, these more complex compounds, particularly the phenolic bodies, are advisedly retained in the methyl alcohol-acetone system. This type of distillate, after separation of a substantial amount of the contained water, is employed as a denaturant mixture and may be added to ethyl alcohol in varying amounts from 0.1 per cent. or less up to 5.0 per cent. or more of the ethyl alcohol which is to be denatured.

Similarly, as indicated hereinbefore, the invention contemplates the utilization of certain selected wood tar distillates as denaturing-gum inhibiting addition agents. Such distillates may be employed alone, but preferably are used in admixture or blend with the crude menthanol fraction.

The crude wood tar, like the crude pyroligneous acid, is a very complex product of which only a relatively few constituents have been identified. It contains many of the constituents of pyroligneous acid, together with "light oils," "heavy oils" and pitch. The "light oils" comprise the fractions boiling below 140° C. and the "heavy oils" comprise the fractions boiling above 200° C. Each of these oil fractions consist of a complex mixture of different types of aliphatic and aromatic compounds. For example, the light oil fraction contains such substances as acetone, methyl ethyl ketone, methyl propyl ketone, methyl butyl ketone, nitriles, di-methyl furane, m-xylene, toluene, and the like. Similarly, the heavy oil fraction comprises a complex mixture of substances comprised largely of phenolic bodies. Such oil fraction contains, for example, phenol, o-, m- and p-cresol, pyrocatechin, pyrogallol, pyrogallol di-methyl ether, propyl pyrogallol di-methyl ether, and the like.

As those skilled in the art know, in the commercial operations of destructive distillation of hardwood, there is, in the earlier stages of separation, no sharp fractionation of the pyroligneous acid from the tars, due to the fact that there is a marked mutual solubility of constituents of each of these two fractions. Thus, in typical American practice, the initial pyroligneous acid layer, which stratifies from the tar in the condenser, usually contains about 7 per cent. or more of the "soluble tars." Conversely, the tar fraction takes up in solution about 6 to 10 per cent., or more, of the pyroligneous acid. It is the common practice to subject the tar fraction to distillation, usually steam distillation, to separate and recover the lighter or volatile fractions. When steam distillation is utilized, certain of the lighter oils come over, together with methyl alcohol, acetone and the like. Such a fraction, when neutralized to remove the acetic acid, constitutes an excellent denaturant under the present invention, in that it comprises a difficultly separable blend of compounds which serve conjointly to denature ethyl alcohol, to more effectively blend such alcohol with gasoline, and to inhibit gum formation in the ultimate fuel.

In carrying out the invention, threfore, selected crude methanol fractions, produced by the destructive distillation of hard woods, are utilized as an addition agent to alcohol intended for employment as a power fuel.

As already indicated, the new denaturing agents may be combined with the alcohol in different manners. For example, as explained, the denaturing composition may first be produced, as for example, by selecting a crude methanol fraction and subjecting this to redistillation or other treatment to largely remove the contained water. In this operation, if desired, the starting material, which is to be concentrated, may be blended with a light tar fraction produced by steam distillation of tar bottoms. The product thus produced may directly be added to the alcohol in substantially any desired proportion, which alcohol may be blended later with gasoline. Again, such a fraction may be added to the alcohol to be employed in the ultimate blend and a given amount of gasoline or other light hydrocarbon oil fraction may be added to the alcohol, so as to secure an intimate blend of alcohol-gasoline concentrate. This concentrated product may then later be used as an addition agent to the gasoline fuel.

Again, if desired, a crude aqueous methanol fraction, of the type described, may be added to the alcohol at certain special stages of production of the latter, particularly during the final concentration of the alcohol. For example, the denaturing composition may be introduced into the stream of alcohol passing from the beer still to the concentration column. In these circumstances, the aqueous denaturant mixture is co-distilled and co-concentrated with the alcohol. Such a method of addition insures an intimate blending of the products by reason of the fact that constituents of the denaturant composition will more readily form azeotropic mixtures with the alocohl to be denatured.

Similarly, if desired, the alcohol denaturant mixture and a portion of the gasoline to be employed in the ultimate fuel may be combined in the one step. This may be done by introducing gasoline into the final concentration tower. The denaturant mixture or concentrate may simultaneously be introduced into the tower, in admixture either with the alcohol or oil stream. In these circumstances, concomitant dehydration of the aqueous denaturant and the aqueous alcohol is effected. During this operation, as will be appreciated, intimately blended azeotropic mixtures of constituents of the denaturant concentrate with the gasoline, on the one hand, and the alcohol, on the other, are produced.

As will be appreciated, the novel denaturing agents contemplated herein produce intimate blends with the gasoline and alcohol base. The denaturant composition is comprised of substances of a wide range of boiling points, within which range is comprehended the boiling point of ethyl alcohol. From such a composition, therefore, it is extremely difficult to sep-

arate the ethyl alcohol. Furthermore, constituents of the denaturant concentrate form wide range of azeotropic mixtures with both alcohol and gasoline. For example, methyl alcohol forms an azeotropic mixture with n-pentane, which mixture has a boiling point of 31° C. Methyl alcohol similarly forms an azeotrope with n-hexane and n-heptane, having boiling points of 60° C. and 65° C., respectively. Again, allyl alcohol forms an azeotrope with n-hexane, having a boiling point of 65.5° C. Yet again, methyl alcohol forms an azeotrope with acetone, boiling at 55.7° C.; methyl alcohol similarly forms an azeotrope with methyl acetate, boiling at 54° C. It will thus be observed that the ultimate composition contemplated herein, i. e., the alcohol-gasoline blend, is comprised of a blended mixture of a broad series of compounds. Due to the fact that the alcoholic and hydrocarbon constituents form azeotropic mixtures with the denaturant concentrate, the entire solution is, so to speak, inextricably blended in that it comprises a whole series of constant boiling mixtures whose boiling points are so close as to substantially preclude separation with any reasonable recovery of alcohol. As will be appreciated also, the presence of these low boiling compounds or mixtures renders the ultimate fuel truly "quick starting."

Furthermore, as will be appreciated, this denaturant concentrate is comprised of constituents which, with respect to the alcohol and the gasoline, are mutual solutes and/or mutual solvents. The concentrate therefore includes a number of excellent blending agents, such as allyl alcohol, alkyl esters, and the like, and this further functions to insure a homogeneous blend of the gasoline with the alcohol.

The denaturant composition, furthermore, includes compounds, particularly phenolic bodies, which act as reducing or gum-inhibiting agents. As pointed out hereinbefore, the proportion of this type of compound in the denaturant concentrate may be adjusted by the selection of predetermined quantities of the tar still distillate. Denaturant concentrates made up according to the present invention are therefore excellent addition agents for the blending of alcohol with gasoline, and particularly cracked gasoline, or other types of fractions which present a decided tendency to gum or sludge formation.

While it has been proposed heretofore to denature ethyl alcohol with methyl alcohol, and while it has also been proposed to add individually functioning blending agents to an alcohol-gasoline blend, it is unexpectable to discover in such cheap, commercially available compounds, as described herein, such an efficacious and multiple functioning adjuvant.

I claim:

1. An improved motor fuel comprising a blend of a preponderant amount of gasoline and a minor amount of ethyl alcohol with which is blended a smaller amount of a dehydrated "light oil" fraction produced by the distillation of hardwood, which fraction is in a quantity sufficient effectively to denature, inhibit gum formation in the fuel and blend the alcohol with the gasoline.

2. An improved motor fuel comprising a blend of a preponderant amount of cracked gasoline and a smaller amount of ethyl alcohol with which is blended a smaller amount of a dehydrated "light oil" fraction produced by the distillation of hardwood, which fraction is in quantity sufficient effectively to denature, inhibit gum formation in the fuel and blend the alcohol with the gasoline.

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