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METHOD OF OBTAINING NITROGENOUS BASES FROM HYDROCARBON MATERIALS.

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My invention relates, in general, to the treatment of hydrocarbon materials, such for example as petroleum or shale oil, for the purpose of obtaining nitrogenous bases.

I have found that nitrogenous bases are present in appreciable quantity in crude gasoline obtained from hydrocarbon materials containing nitrogenous compounds.

By my method I first secure from the hydrocarbon material a crude gasoline, which may be defined and identified as all the material boiling up to and including 450° F. approximately, and which has had no treatment except distillation. Any method commonly known in the art may be employed to secure this crude gasoline. Although gasoline is a term which is quite broadly used and may include products the properties of which vary considerably, I may state that the material which, in carrying out my method I wish initially to secure, and which I call crude gasoline, is the first distillation from crude oil having a maximum boiling point of 450° F. approximately.

I do not, however, confine myself to crude gasoline obtained by a simple distillation from crude oil, for it may be done by other methods, as by cracking, or distillation under pressure; and also crude gasoline may be secured from shale oil, or cracked shale oil. But in any case the crude gasoline on which I work may be considered, as defined above, as all of the material boiling up to and including 450° F. approximately, and which has had no treatment other than distillation.

Having secured the crude gasoline, the next step in my method is to bring it into intimate contact with a suitable reagent, preferably an acidic substance as, for example, sulphuric acid containing 25% H_2SO_4, and then separate the reaction product or acidic material which contains substantially all of the nitrogenous bases in the form of sulphates.

In cases where sulphur compounds are present in considerable quantities, I have found it desirable to first treat the crude or raw gasoline with a suitable solution, for example, caustic soda, to remove the majority of these sulphur compounds, prior to treatment with the reagent or dilute acid.

While I choose to employ dilute sulphuric acid as a convenient material for removing nitrogenous bases, any reagent whether acidic or not may be employed, for example, other acids or combinations thereof or clays or combinations of acids and clays which also have the property of combining with nitrogenous bases, may be used.

The treatment with dilute acid may be conducted in a suitable counter-flow apparatus so that the gasoline after passing through is substantially free from nitrogenous compounds and the acidity of the acid liquor substantially neutralized by the bases it absorbs.

This is the ultimate condition desired, although it is not necessary to adjust the treatment to exactly accomplish this. For example, treatment might be conducted so that the acid will have lost only half its strength due to combination with the nitrogenous bases from the gasoline.

When the acid liquor contains the desired amount of nitrogenous bases, its excess acid is completely neutralized and the nitrogenous bases freed by the addition of an excess of caustic alkali, as, for example, caustic soda.

This alkaline liquor is then distilled, preferably accompanied with injection of steam into the liquor. The distillate from such distillation consists, in general, of two parts, viz:—nitrogenous bases insoluble in water, which being lighter than water float on it in oily form, and the water solution consisting of steam condensate and soluble nitrogenous bases.

I have found that there are two types of nitrogenous bases recoverable from gasoline, viz:—those soluble in water and those insoluble in water. The bases insoluble in water are separated from the distillate and are dried for use. The water portion distillate, which contains an appreciable quantity of nitrogenous bases soluble in this medium, is made acid and concentrated to small volume by evaporation. To this evaporated liquor is then added an excess of alkali. When the nitrogenous bases separate and come to the top they are removed and thoroughly dried, after which they may be subjected to distillation for purification.

The nitrogenous bases herein referred to may be defined as a mixture of basic compounds of carbon, hydrogen and nitrogen, of which the larger proportion is composed of

nitrogen bases with nitrogen in the ring; as for example, pyridine, quinoline, and piperidine, and homologues thereof. Relatively small amounts of pyrrol and amino derivatives are also present in some cases in the crude material. Generally speaking, the product is an oily liquid, soluble in acid and insoluble in alkali. It precipitates with silico-tungstic acid from acid solution. Analysis of the recovered nitrogenous bases by the standard silico-tungstic method for nicotine shows from 30% to 50% calculated as nicotine. These nitrogenous bases may be used, among other things, as an insecticide.

I cite an example of one way in which nitrogenous bases may be obtained by this process: 5000 gallons of crude gasoline were first passed through 15 gallons of a 20 Baumé solution of caustic soda for the removal of objectionable compounds. The gasoline was next passed through 2 gallons of a solution of sulphuric acid containing 25.46% of H_2SO_4. The acid liquor which had absorbed substantially all of the nitrogenous bases from the gasoline was then removed. Examination of the acid liquor disclosed that its acidity had been reduced from 25.46% H_2SO_4 to 11.50% H_2SO_4. The acid liquor was then made strongly alkaline by the addition of an excess of caustic soda and distilled with steam. From this distillation there was obtained 150 c. c. of nitrogenous bases insoluble in water. An analysis of these bases showed them to contain 8.41% nitrogen and a boiling point range of 260° F. to 520° F. The water portion of the distillate was made acid and this acid liquor concentrated by evaporation to approximately 5000 c. c. This concentrated portion of the distillate, containing the sulphates of the bases soluble in water, was then made strongly alkaline, causing the free nitrogenous bases to separate and come to the surface of the liquor, from which they were removed and dried for use, the quantity obtained being 45 c. c. On analysis these nitrogenous bases showed 9.32% of nitrogen.

I claim:—

1. The method of obtaining nitrogenous bases which comprises obtaining from a hydrocarbon material a crude gasoline; treating said crude gasoline with an acidic reagent to form compounds with the nitrogenous bases; separating the acid liquor resulting from said treatment; neutralizing the excess acid to free the nitrogenous bases, by the addition of an excess of an alkali; distilling said alkaline liquor in the presence of water to separate the nitrogenous bases in two types, soluble and insoluble, respectively, in water; removing the insoluble type; concentrating the liquor containing the soluble type; adding to said concentrated liquor an excess of alkali; and separating the nitrogenous bases therefrom.

2. The method of obtaining nitrogenous bases which comprises obtaining a crude gasoline from a hydrocarbon material; treating said crude gasoline with a reagent to form compounds with the nitrogenous bases; separating the reaction compound; making said reaction compound alkaline; distilling the alkaline liquor containing said compounds to separate the nitrogenous bases in two types, soluble and insoluble, respectively, in water; separating said types, one from the other, in accordance with their differential solubility.

In testimony whereof I have signed my name to this specification.

HARRY K. IHRIG.