Patented June 28, 1932 1,865,235

UNITED STATES PATENT OFFICE

ROY CROSS, OF KANSAS CITY, MISSOURI, ASSIGNOR TO CROSS DEVELOPMENT CORPORATION, OF WILMINGTON, DELAWARE, A CORPORATION OF DELAWARE

TREATING PROCESS FOR HYDROCARBON OILS

No Drawing. Application filed June 28, 1926. Serial No. 119,171.

This invention relates to improvements in the process of refining petroleum oils such as gasoline, medicinal oil, lubricating oils, industrial naphtha, machine oils and the like. It more particularly relates to the purification of hydrocarbon oils or oils consisting largely of hydrocarbons. Among its purposes are the following:

1. For removal of sulphur.
2. For removal of color and to produce water white products.
3. For removal of obnoxious odors.
4. For stabilizing the oil as to color and odor.

In the practice of this invention metals or the hydrides of metals of the alkali and alkali earth group are used. These metals include, in their order of usefulness and availability—metallic sodium, metallic calcium, metallic potassium, metallic magnesium, metallic strontium, metallic barium, metallic lithium.

Some of the important properties in considering this invention may be tabulated as follows:

Metal	Combining equivalent	Melting point	Specific gravity
		°C.	
Sodium	23	97.6	0.971
Calcium	20	805	1.54
Potassium	39.1	63.5	0.862
Magnesium	12	650	1.70
Barium	68	850	3.78

It has been found that all of these metals and their hydrides react with petroleum oil to effect a removal of sulphur, a removal of color, a polymerization of unsaturated compounds and a stabilization of the hydrocarbons to a more or less variable degree. As to sulphur removal, the alkali metals, such as potassium and sodium, are very active, though magnesium and calcium are more effective quantitatively. In other words, 12 parts of magnesium, 20 parts of calcium, 39 parts of potassium and 23 parts of sodium have the capacity for combining with the same amount of sulphur.

The method of application of the metal or the metal hydride will vary slightly in each case. Ordinarily, higher temperatures are required to effect desulphurization with the alkali earth metals than with the alkali metals. The method of application will, of course, vary in each case. In some instances it is desirable to use a combination of the metals. This is particularly well illustrated in the use of mixtures of metallic sodium and metallic potassium. Although the melting point of metallic sodium is approximately 97° C. and of metallic potassium approximately 63° C., a mixture of two gram molecules of potassium with 1 gram molecule of sodium has a melting point of 10° C. below zero. All intermediate temperatures can be obtained by using the appropriate percentages. In the same way mixtures of alkali metals and alkali earth metals can be used to give products of low melting point. Products or appropriate melting point can be made to correspond with the temperatures at which it is desired to treat the hydrocarbon. For example, if it is desired to treat very light gasoline, a mixture of potassium and sodium having a melting point of 0° C. may be used and the gasoline may be bubbled directly through the metal mixture, or the metal mixture may be made to flow in opposite direction and in contact with the flow of the hydrocarbons. The sulphides or precipitates formed in the metal can then be continuously removed from the system and purified to return only the pure metal.

There is a great variety of ways of applying these metals or metal hydrides for the removal of sulphur, color and to otherwise purify hydrocarbon oils. Some of the important methods may be classified as follows:

1. The metal is contacted either hot or cold and either with the hot liquid or the hot vapor of the oil to be treated. A suitable method of contacting is to first mix the metal thoroughly with a heated bleaching clay or other distributing material and then use this material for treating the vapors or the liquid oil. This material may be applied either by passing the vapors through the metal treated clay in a tower or by mixing the clay with the liquid oil and filtering off the metal mixed clay.

One suitable method in the treating of

cracked gasoline is to contact the gasoline fairly quickly with sulphuric acid of a gravity usually of from 60° to 65° Bé. The acid is then very quickly removed, preferably by the use of a centrifuge. The gasoline is then continuously mixed with the metal coated clay which is quickly pumped through a filter press such as a Sweetland filter. The product is largely desulphurized, has a fairly good odor and has a water white color. As a general rule, however, the higher the temperature of treatment the more complete is the sulphur removal, although it is not necessary to use the higher temperatures to get a good bleaching effect. For complete sulphur removal it is necessary to have sufficient metal to react with all of the sulphur. It is, of course, always important to eliminate insofar as possible any water or steam from the oil before treating. This method of treatment applies to other oils, such as lubricating oils, painter's naphtha and the like where good color and low sulphur content are desirable.

2. The treatment may also be applied by pumping the liquid or vapor directly over the metal in granular form. This metal may be granulated by melting and the unused metal may be recovered by remelting and removing the impurities, the treatment, however, being effected on the surface of the metal in solid condition.

3. In many instances treatment may be effected by bubbling the liquid through the molten metal or mixtures of metals. This method of treatment is convenient as it can be carried out in completely enclosed containers, and also will allow the circulation of the metal as well as the hydrocarbon oil and in counterflow to each other. This treatment may be effected at almost any desired temperature as alloys or mixtures can be made having melting points from 10° C. below zero up.

In the treatment of hydrocarbon oils with alkali and alkali earth metals it has been possible to remove a varying percentage of the sulphur. The sulphur exists in the oil in a number of different combinations, including such substances as—

Mercaptans, thio-alcohols or alkyl hydrosulphides=RHS

Alkyl disulphides=R_2S

Sulphine or sulphonium compounds=R_3SCl

Sulphones=R_2SO_2

Sulphonic acids=$RHSO_3$

Thio-sulphonic acids=RHS_2O_2

Sulphinic acids=$RHSO_2$

The amount of sulphur removed has varied in different types of oils from 10% to 95%. This varies also with the method of treatment and the particular metal used. Potassium and sodium metals and potassium and sodium hydrides are most effective at lower temperatures, although at higher temperatures calcium is very effecive. Magnesium is apparently least effective of all, although in some instances it is more effective for color removal than the other metals.

It is not perfectly clear just how these metals effect so complete removal of the sulphur without destroying the molecule, but the low percentage of loss, in most cases being much less than 3%, indicates that the sulphur is extracted from the molecule and the hydrocarbon portion of the molecule either forms a new molecule or undergoes a rearrangement of the hydrogen atoms. Probable reactions may be shown by the following symbolic reactions, assuming M to represent the metal, H to represent the hydrogen and R to represent the hydrocarbon radical involved. The reaction of a mercaptan would be approximately as follows:

$$RSH+M=RH+MS$$

or, as a specific instance using ethyl mercaptan or sulphhydride,

$$C_2H_5SH+Ca=C_2H_6+CaS$$

In the case of an alkyl sulphide reaction might be as follows:

$$RS+MH=MS+RH$$

or, in the case of an alkyl disulphide:

$$R_2S+M=R-R+MS$$

In this latter case, there of course might in some instances be very complex polymerization.

This method of treating is particularly applicable to cracked gasolines, since such gasolines have a larger percentage of sulphur than normally distilled gasoline. Furthermore, the sulphur in such gasoline is in a more resistant condition to ordinary treating methods. The usual specification requires that gasoline of this nature have not more than one-tenth of one percent of sulphur, whereas cracked gasoline in its raw state frequently has from 0.2% to 1% of sulphur. By the ordinary methods of refining with sulphuric acid all of the molecule combined with the sulphur is removed, thus entailing a loss of often as much as 40% of the gasoline when it is desired to produce a product having less than one-tenth of one per cent of sulphur. With this method of treatment, however, the loss in extreme instances would rarely exceed 5%. California gasoline is particularly hard to treat and by this method it has been found possible to remove in most instances from 50% to 90% of the sulphur in the gasoline without any substantial losses of volume.

I claim as my invention:

1. A method of treating petroleum, which consists in continuously passing the petroleum in intimate contact with a metal of the alkaline earth group in a liquid state, the said

metal caused to flow in an opposed direction to the direction of flow of the petroleum to effect a chemical combination with said metal, continuously removing and purifying the metal, and continuously removing and cooling the petroleum.

2. A method of treating petroleum, which consists in continuously passing the petroleum vapors in intimate contact with a liquid alkaline earth metal, the liquid metal passing in an opposed direction to the direction of flow of the petroleum to effect a chemical combination with said metal, continuously removing and purifying the metal, and continuously removing and cooling the petroleum.

3. A method of treating petroleum oil which consists in continuously passing the petroleum in intimate contact with metallic calcium, the calcium being heated above its melting point, the calcium passed in an opposed direction to that of the flow of the petroleum oil to effect a chemical combination between the calcium and the impurities in said oil, and removing the purifying metal and continuously removing and cooling the treated oil.

4. A method of treating petroleum oil which consists in continuously passing the petroleum in intimate contact with metallic calcium, the calcium being heated above its melting point, the calcium passed in an opposed direction to that of the flow of the petroleum oil to effect a chemical combination between the calcium and the impurities in said oil, continuously removing the purifying metal and continuously removing the purified oil from the system.

5. The method of desulphurizing and decolorizing hydrocarbon oil, including the step of contacting said oil with an alkaline earth metal to effect a chemical combination between said alkaline earth metal and the sulphur compounds to be eliminated.

6. The method of desulphurizing and decolorizing hydrocarbon oil, including the steps of contacting said oil with an alkaline earth metal to effect a chemical combination between said alkaline earth metal and the sulphur compounds to be eliminated, continuously removing the chemical compounds thus formed.

7. The method of desulphurizing and decolorizing hydrocarbon oil, including the steps of contacting said oil with an alkaline earth metal to effect a chemical combination between said alkaline earth metal and the sulphur compounds to be eliminated, continuously removing the chemical compounds thus formed and subsequently recovering said metal from said compound.

8. The method of desulphurizing and decolorizing hydrocarbon oil, including the step of contacting said oil with an alkaline earth metal in comminuted form to effect a chemical combination between said alkaline earth metal and the sulphur compounds to be eliminated.

9. The method of desulphurizing and decolorizing hydrocarbon oil, including the step of contacting said oil with an alkaline earth metal, incorporated with an argillaceous material, to effect a chemical combination between said alkaline earth metal and the sulphur compounds to be eliminated.

10. The method of desulphurizing and decolorizing hydrocarbon oil, including the steps of contacting said oil with an alkaline earth metal, incorporated with an argillaceous material, to effect a chemical combination between said alkaline earth metal and the sulphur compounds to be eliminated, and continuously removing the compounds thus formed.

11. The method of desulphurizing and decolorizing hydrocarbon oil, including the steps of contacting said oil with an alkaline earth metal, incorporated with an argillaceous material, to effect a chemical combination between said alkaline earth metal and the sulphur compounds to be eliminated, continuously removing the compounds thus formed, and subsequently removing said metal from said compound.

12. The method of desulphurizing and decolorizing hydrocarbon oil which includes the steps of continuously passing the oil in a vapor phase, in contact with an alkaline earth metal in liquid form to effect a chemical combination between said alkaline earth metal and the impurities to be eliminated from said hydrocarbon, resulting in a precipitate of said combination, and continuously removing said precipitate.

13. A process as in claim 12 in which the hydrocarbon flows in a direction counter to the alkaline earth metal in liquid form.

14. A process as in claim 5 in which the alkaline earth metal is calcium.

15. A process as in claim 5 in which the alkaline earth metal is barium.

16. A process as in claim 5 in which the alkaline earth metal is magnesium.

17. A continuous method of purifying petroleum hydrocarbons including the steps of vaporizing the hydrocarbons and bringing the evolved vapors into intimate contact with an alkaline earth metal in a liquid state, continuously circulating said liquefied alkaline earth metal in counter flow relation with said hydrocarbon vapor, to form polymers by chemical action, diverting saturated polymers and reaction products and supplying additional unused treating metal.

ROY CROSS.