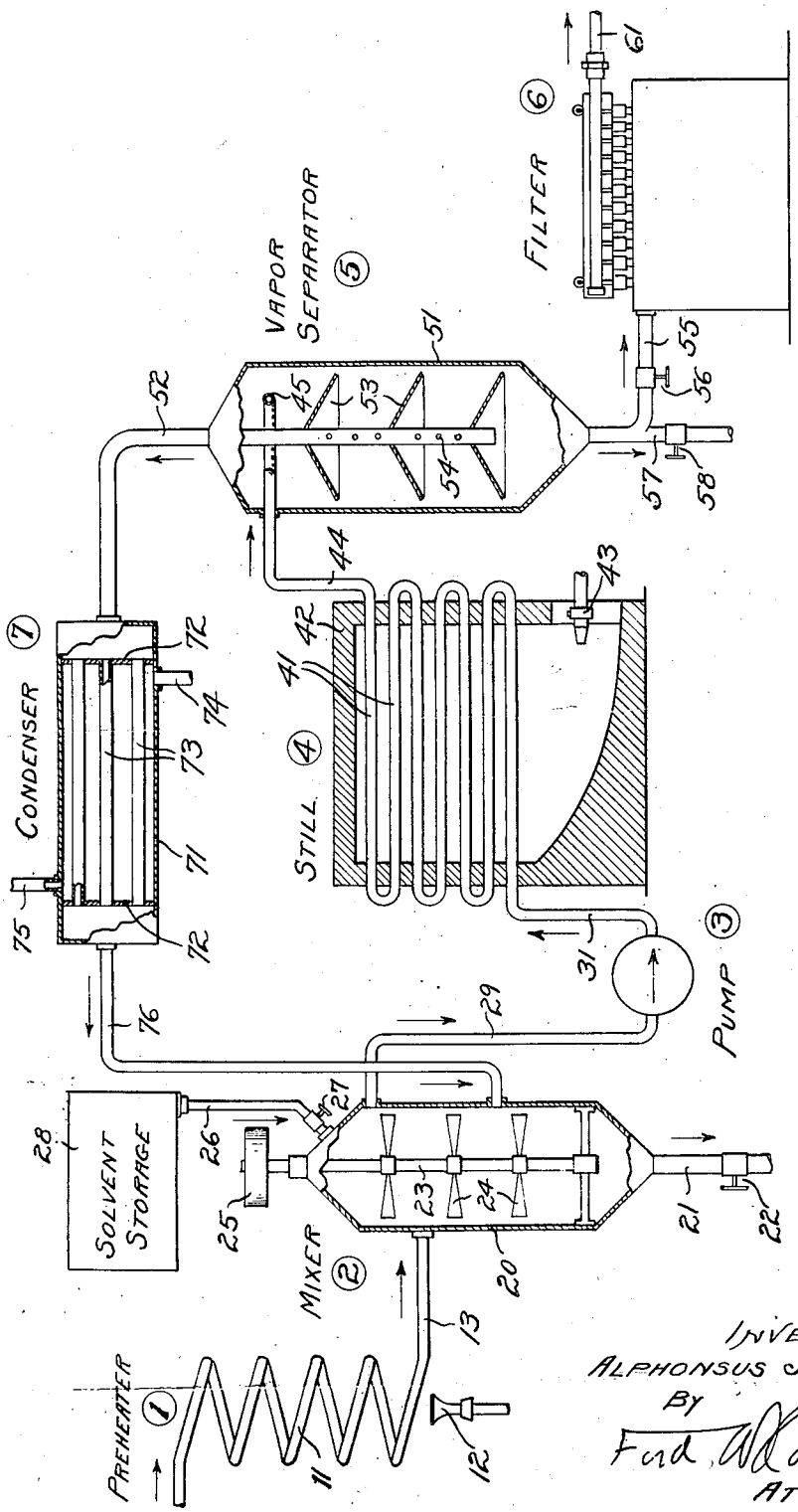
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METHOD OF ELIMINATING COLLOIDAL ASPHALTENES AND CARBENES FROM FUEL OIL

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METHOD OF ELIMINATING COLLOIDAL ASPHALTENES AND CARBENES FROM FUEL OIL

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My invention relates to the art of oil refining. In that art it is common practice to subject petroleum oils and distillates to heat and pressure for the purpose of producing volatile or low boiling point hydrocarbons, such as gasoline, this operation being commonly termed "cracking". In the cracking operation certain overhead distillates are produced, leaving a liquid residuum. This liquid residuum consists of high boiling point material which is commonly used as fuel oil.

In the operation of certain well known types of cracking plants, considerable quantities of such residuum are produced; but this residuum contains substances which render the residuum unsuitable for ordinary use as a fuel oil. These substances can be conveniently, although perhaps rather arbitrarily, divided into asphaltenes, carbenes, and free carbons. The asphaltenes are insoluble at atmospheric temperatures in petroleum-ether but soluble in carbon-tetrachloride and benzene. The carbenes are insoluble at atmospheric temperatures in petroleum-ether and carbon-tetrachloride, but are soluble in benzene. The free carbon is, of course, insoluble at all temperatures in any ordinary solvent. There is no sharp line of demarcation between these three classes, some carbenes differing only slightly from free carbon and some asphaltenes being similar in properties to the carbenes.

I have found that residuums produced by cracking often contain all three classes of substances but that the proportion of each and the physical properties of the residuums so produced vary widely even in the operation of the same apparatus on the same oil.

The asphaltenes, carbenes and carbon are objectionable, since they tend to settle out of the oil, forming heavy adherent materials which clog up the piping and burners of the fuel oil plants in which they are used. So strong, in fact, is the prejudice against them that it is common practice to test fuel oils by centrifuging a mixture of equal parts of benzol and the oil to be tested, and such a test ordinarily discloses large amounts of asphaltenes, carbenes and carbon in all cracked residuums. Some such residuums showing a high proportion of colloidal and solid matter, while actually quite suitable for use as fuel oil, since the suspended matter does not readily settle out, are nevertheless unsalable due to the poor showing made when tested as above described. It is, therefore, of great importance to free the residuum from these suspended solids and colloids, and it is an object of my invention to provide a means for so doing.

I have found that it is possible to remove the suspended free carbon by filtration, but if this carbon is associated or combined with colloidal asphaltenes, and carbenes, it is not commercially feasible to operate filters which quickly clog up due to the accumulation of colloidal matter therein. It is a further object of my invention to so treat a cracked residuum that the colloids are physically changed into a form that will readily pass through a filter, which catches and removes the free carbon.

I am now inclined to believe that the asphaltenes and carbenes consist of free carbon combined or associated with hydrocarbons, and that due to the peculiar nature of the combination the resulting substances are insoluble in the oil in which they are carried. I have found, however, that by treating these substances with powerful solvents, I can apparently break the bond between the carbon and the hydrocarbon, and that, once this has been done, the hydrocarbon goes readily into solution in the original oil and remains in such solution even if the solvent is then distilled off.

I have found that the asphaltenes and carbenes, while apparently not soluble in the petroleum oil in which they are found, are nevertheless soluble in hot petroleum-ether, and that after the evaporation of the petroleum-ether there is left a substance almost completely soluble in the original oil.

Further objects and advantages will be made evident hereinafter.

The annexed drawing shows diagrammatically partly in section an apparatus for practicing my invention. In this drawing I provide a preheater 1, a mixer 2, a pump 3, a

still 4, a vapor separator 5, a filter 6, and a condenser 7.

When operating my invention directly in connection with a cracking plant, it is unnecessary to provide the preheater 1, the hot residuum being delivered directly into the mixer 2 from the cracking still. Where it is desired to treat cold fuel oil or residuum, the preheater 1 is provided and it may consist of a coil 11 of any convenient form heated by a burner 12, the heated oil being delivered through a pipe 13 into the mixer 2.

The mixer 2 consists of a tight shell 20 having a coned bottom terminating in a dumping pipe 21, normally closed by a valve 22 and used only to clean the mixer at long intervals. Mounted on a shaft 23 inside the shell 20 is a plurality of paddles 24, the shaft 23 extending upwardly through the top of the shell 20 and being provided with a pulley 25 which may be driven from any suitable source of power (not shown). A solvent inlet pipe 26, having a valve 27, delivers solvent from a suitable storage tank 28 into the mixer 2. Fluid is delivered from near the top of the mixer 2 through a pipe 29 to the pump 3.

The pump 3 may be of any convenient form and it delivers liquid through a pipe 31 to the still 4.

The still 4 may be of the form shown, consisting of a plurality of tubes 41 passing through a furnace 42 heated by any convenient means, such as the oil or gas burner 43. Fluid is delivered from the still 4 through a pipe 44 to a ring of pipe 45 having perforations therein situated in the top of the vapor separator 5.

The vapor separator 5 consists of a tight shell 51 having a central vapor outlet pipe 52. Carried on the pipe 52 within the shell 51 is a plurality of spreader cones 53. The lower end of the pipe 52 is open and perforations 54 are provided in the pipe 52 between the cones 53. Vapor is taken off through the pipe 52 and liquid is delivered through a pipe 55 to the filter 6.

The filter 6 may be of any convenient form and serves to separate solid material from the oil delivered through the pipe 55, cleaned oil being delivered through a pipe 61 to suitable storage.

The pipe 55 is provided with a valve 56 and connects with a pipe 57 having a valve 58.

Vapor is delivered by the pipe 52 into the condenser 7 which may be of any convenient form, that shown consisting of a tight sheel 71 having intermediate heads 72, between which tubes 73 extend. Vapors pass through the tubes 73, the space around the tubes 73, between the heads 72, being filled with cooling water delivered by a pipe 74, heated water being taken off by a pipe 75. The condensates from the condenser 7 are delivered by a pipe 76 into the mixer 2.

A convenient method of operating my invention is as follows:

The mixer 2 being partially filled with solvent from the tank 28 through the pipe 26, hot residuum from the cracking still (not shown), or from the preheater 1, is run into the mixer 2 through the pipe 13. The residuum and solvent are thoroughly mixed by the paddles 24 and the mixture is delivered by the pipe 29 to the pump 3 and forced by the pump 3 into the still 4.

In practice I may use any suitable solvent, such as carbon-tetrachloride, petroleum-ether or other petroleum distillate. In practice I prefer to maintain the mixer 2 at a temperature below the boiling point of the solvent. In the still 4 I heat the mixture delivered thereto by the pipe 31 to such a temperature that all the solvent is vaporized, the pipes 44 and 45 delivering the mixture in the form of foam into the top of the vapor separator 5. This foam is spread by the upper cone 53, passing downwardly along the inner wall of the shell 51. During its downward passage, the solvent is vaporized, passing upwardly through the pipe 52 to the condenser 7, where it is condensed, being then delivered as a hot condensate through the pipe 76 to the mixer 2.

By a suitable regulation of temperatures, I am able to separate substantially all of the solvent from the residuum and to return it to the mixer 2, so that very little solvent need be supplied from the solvent tank 28 during the operation of my invention.

The separated residuum is delivered from the separator 5 through the pipe 55 to the filter 6, or through the pipe 57 to suitable storage.

The oil delivered through the pipe 57 is substantially free from colloidal asphaltenes or carbenes, and the free carbon is in such form that it can be readily filtered out in the filter 6, so that the oil delivered through the pipe 61 is substantially free from colloidal asphaltenes and carbenes, and free carbon.

I am inclined to think that the asphaltenes and carbenes are in reality colloidal combinations of carbon and hydrocarbons.

While I do not wish to be understood as definitely committing myself as to any theory of the operation of my invention, I believe the following is a probable one.

My invention probably depends upon the fact that the asphaltenes and carbenes, while insoluble in cold petroleum of high boiling point, are readily dissolved in hot petroleum of lower boiling point, or in carbon-tetrachloride or other solvents, and that the resulting solution is itself readily soluble in cold petroleum of high boiling point. As a result, it is possible to dissolve a portion of the asphaltenes and carbenes by hot solvents; and when so dissolved, to dissolve them in the oil in which they were previously suspended.

We may consider the asphaltenes and carbenes as made up of carbon or other petroleum insoluble material, colloidally associated with material which is normally soluble in the petroleum in which it is suspended, but which from its colloidal nature or the nature of its associated insoluble material, is prevented from going into solution in such petroleum. Upon mixing the petroleum and its suspended colloids with a suitable solvent, the soluble portion of the colloids is dissolved, perhaps first in the solvent and then in the petroleum, so that upon the removal of the solvent by heat the soluble portion of the colloid is left in solution in the petroleum and the insoluble portion appears as free suspended carbon.

Whatever may be the theory of operation I have found that by treating cracked residuums as described, some very remarkable results are produced.

For example, I have found that some residuums show as high as 32 per cent of colloidal and solid material when centrifuged with an equal part of benzol. This colloidal and solid material in one particular sample showed about 12 per cent coke when extracted with benzol. Other samples of the same material were found to contain 87.4 per cent of matter soluble in carbon-tetrachloride, 86.4 per cent of matter soluble in benzene, and 69.5 per cent of matter soluble in petroleum-ether. By treating this particular residuum, which initially contained 32 per cent of colloidal and solid matter, with carbon-tetrachloride, which was then distilled off, I produced an oil containing less than 6 per cent of colloidal and solid matter which was in such a condition as to readily filter out.

This is not an exceptional case and in fact I have been able in some cases by the use of my invention, treating a residuum containing 30 per cent of colloidal and solid matter, to reduce this matter to less than 2 per cent without filtration. Such a product is commercially satisfactory without filtration.

I have also found that comparatively small proportions of solvent are sufficient in many cases, the mixture delivered to the still containing less than 20 per cent of solvent.

I have also found that although carbon-tetrachloride and other relatively expensive solvents give superior results, it is commercially feasible to operate using as solvents the lighter petroleum distillates produced commercially in large quantities in many large oil refineries.

By my invention I am able to very cheaply treat what are now regarded as most undesirable residues to produce acceptable fuel oils. In so doing I do not find it necessary to reduce the bulk of the oil by entirely removing the colloidal and solid matter carried therein, but on the contrary I merge the larger part of this matter into the fuel oil itself. My process is, therefore, superior to any filtration process in which all the asphaltenes and carbenes might be removed, in that it converts the useless substances into fuel oil.

My invention also has a special utility in that it is particularly well suited to handle oils having a relatively low free carbon content but containing a large proportion of asphaltenes and carbenes. Previous to my invention such oils were substantially useless even as fuel oils. No method was known of treating them to remove the asphaltenes and carbenes, which could not be successfully filtered out due to their viscous or colloidal nature and which settled out very slowly if allowed to stand. Such oils which showed perhaps as high as 30 per cent of colloidal and solid matter were, therefore, not salable in their original form due to their sludge test, and could not be successfully treated to make them salable. By my invention such oils can generally be so treated as to be readily salable and in many cases this can be accomplished without filtration.

I claim as my invention:

1. A process of treating cracking residues of petroleum oils, containing particles of substantially free carbon, which tend to adsorb liquid hydrocarbons in the nature of colloidal asphaltenes and carbenes, and to settle out from the residue in the form of sludge, for the purpose of reducing the quantity of material so adsorbed or liable to be adsorbed, comprising: adding to the cracking residue a sufficient quantity of a lighter petroleum distillate capable of dissolving asphaltenes and carbenes, mixing both materials and keeping the mixture at an elevated temperature, not over the boiling point of the lighter petroleum distillate, for a sufficient time to remove most of the asphaltenes and carbenes from the free carbon, dissolving them in the balance of the cracking residue, and removing the mixture to storage.

2. A process of treating cracking residues of petroleum oils, containing particles of substantially free carbon, which tend to adsorb liquid hydrocarbons in the nature of coloidal asphaltenes and carbenes, and to settle out from the residue in the form of sludge, for the purpose of reducing the quantity of material so adsorbed or liable to be adsorbed, comprising: adding to the cracking residue a sufficient quantity of a lighter petroleum distillate obtained from a cracking process, and capable of dissolving asphaltenes and carbenes, mixing both materials and keeping the mixture at an elevated temperature, not over the boiling point of the lighter petroleum distillate, for a sufficient time to remove most of the asphaltenes and carbenes from the free carbon, dissolving them in the balance of the

cracking residue, and removing the mixture to storage.

3. A process of treating cracking residues of petroleum oils, containing particles of substantially free carbon, which tend to adsorb liquid hydrocarbons in the nature of colloidal asphaltenes and carbenes, and to settle out from the residue in the form of sludge, for the purpose of reducing the quantity of material so adsorbed or liable to be adsorbed, comprising: adding to the cracking residue a sufficient quantity of a lighter petroleum distillate capable of dissolving asphaltenes and carbenes, mixing both materials and keeping the mixture at an elevated temperature, not over the boiling point of the lighter petroleum distillate, for a sufficient time to remove most of the asphaltenes and carbenes from the free carbon, dissolving them in the balance of the cracking residue, filtering off from the mixture substantially only the solid granular carbon material, and removing the mixture to storage.

4. A process of treating cracking residues of petroleum oils, containing particles of substantially free carbon, which tend to adsorb liquid hydrocarbons in the nature of colloidal asphaltenes and carbenes, and to settle out from the residue in the form of sludge, for the purpose of reducing the quantity of material so adsorbed or liable to be adsorbed, comprising: adding to the cracking residue a sufficient quantity of petroleum ether capable of dissolving asphaltenes and carbenes, mixing both materials and keeping the mixture at an elevated temperature, not over the boiling point of the petroleum ether, for a sufficient time to remove most of the asphaltenes and carbenes from the free carbon, dissolving them in the balance of the cracking residue, and removing the mixture to storage.

5. A process of treating cracking residues of petroleum oils, containing particles of substantially free carbon, which tend to adsorb liquid hydrocarbons in the nature of colloidal asphaltenes and carbenes, and to settle out from the residue in the form of sludge, for the purpose of reducing the quantity of material so adsorbed or liable to be adsorbed, comprising: adding to the cracking residue a sufficient quantity of a lighter petroleum distillate capable of dissolving asphaltenes and carbenes, mixing both materials and keeping the mixture at an elevated temperature, not over the boiling point of the lighter petroleum distillate, for a sufficient time to remove most of the asphaltenes and carbenes from the free carbon, dissolving them in the balance of the cracking residue, distilling off the lighter petroleum distillate, filtering off from the residue substantially only the solid granular carbon material, and removing the residue to storage.

6. A process of treating cracking residues of petroleum oils, containing particles of substantially free carbon, which tend to adsorb liquid hydrocarbons in the nature of colloidal asphaltenes and carbenes, and to settle out from the residue in the form of sludge, for the purpose of reducing the quantity of material so adsorbed or liable to be adsorbed, comprising: adding to the cracking residue a sufficient quantity of a lighter petroleum distillate capable of dissolving asphaltenes and carbenes, mixing both materials and keeping the mixture at an elevated temperature, not over the boiling point of the lighter petroleum distillate, for a sufficient time to remove most of the asphaltenes and carbenes from the free carbon, dissolving them in the balance of the cracking residue, distilling off the lighter petroleum distillate, condensing and returning this distillate for reuse to the mixing chamber, filtering off from the residue substantially only the solid granular carbon material, and removing the residue to storage.

In testimony whereof, I have hereunto set my hand at Martinez, California, this 14th day of January, 1925.

ALPHONSUS JURRISSEN.