R. DE M. TAVEAU.

PETROLEUM PRODUCT AND PROCESS OF MAKING THE SAME.

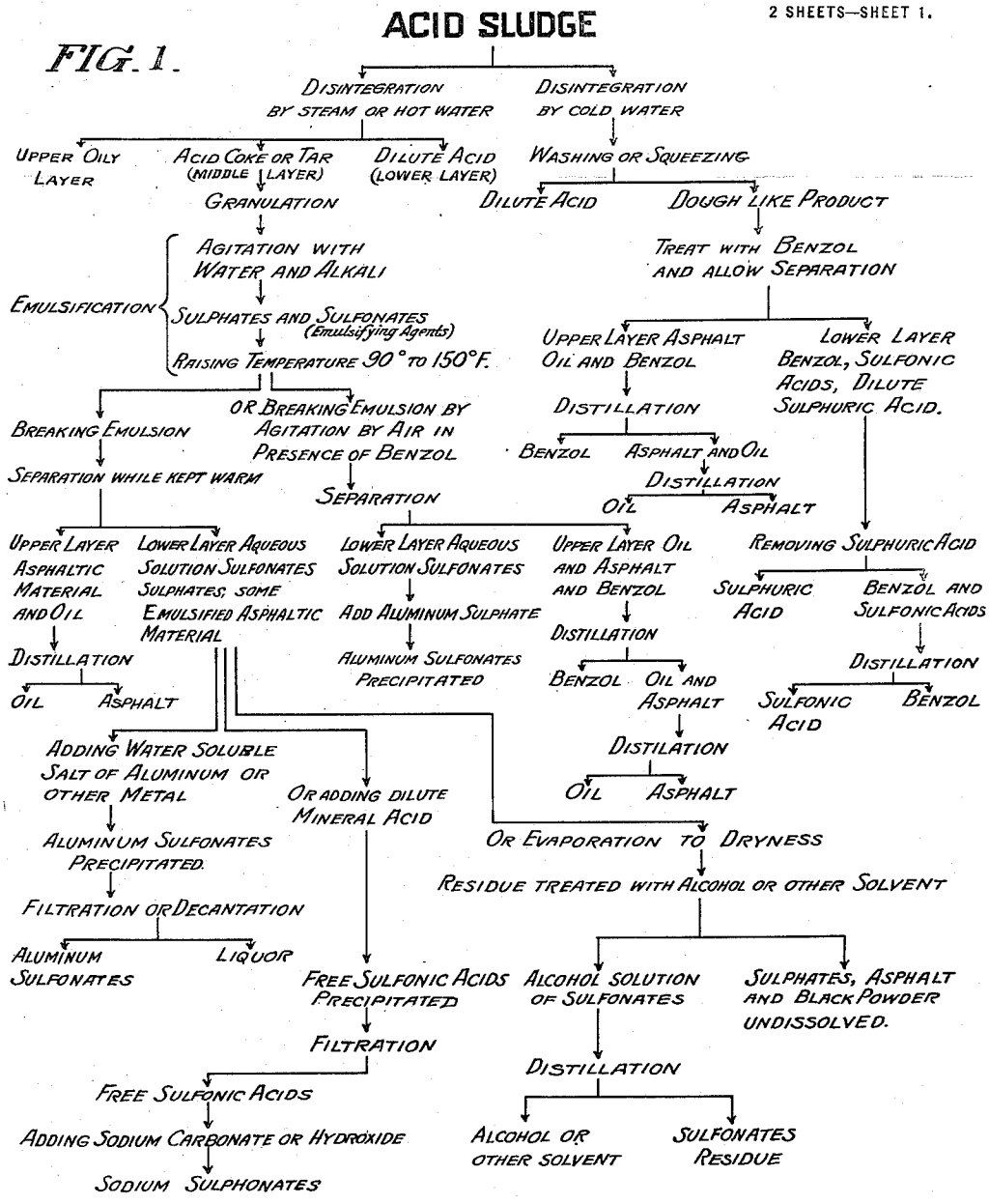
APPLICATION FILED JULY 6, 1914.

1,271,387.

Patented July 2, 1918.

2 SHEETS—SHEET 1.

FIG. 1.



WITNESSES

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William Conway.

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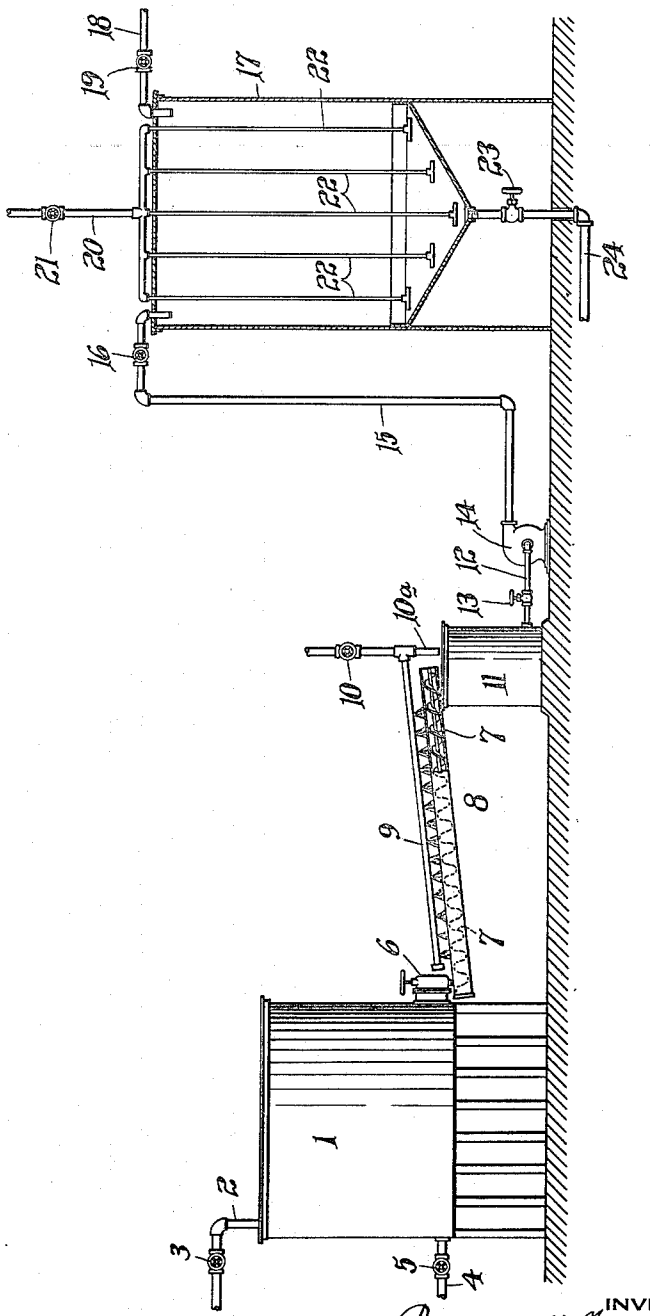


FIG. 2.

WITNESSES

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UNITED STATES PATENT OFFICE.

RENE DE M. TAVEAU, OF PHILADELPHIA, PENNSYLVANIA, ASSIGNOR TO THE ATLANTIC REFINING COMPANY, OF PHILADELPHIA, PENNSYLVANIA, A CORPORATION OF PENNSYLVANIA.

PETROLEUM PRODUCT AND PROCESS OF MAKING THE SAME.

1,271,387. Specification of Letters Patent. **Patented July 2, 1918.**

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To all whom it may concern:

Be it known that I, RENÉ DE M. TAVEAU, a citizen of the United States, residing in the city of Philadelphia, county of Philadelphia, and State of Pennsylvania, have invented new and useful Petroleum Products and Processes of Making the Same, of which the following is a specification.

My invention resides in a process of treating certain products resulting from acid treatment of petroleum, petroleum distillates or residua remaining after distillation of petroleum for recovering or deriving therefrom an emulsion, asphalt, oil, sulfonic acids or sulfonates; and my invention resides in these products resulting from such process.

Whenever crude petroleum, petroleum distillate or the residuum remaining after distillation of crude petroleum is brought into contact with concentrated sulfuric acid, 50° Bé. or stronger, including fuming sulfuric acid, or some other suitable sulfonating agent, as chlorsulfonic acid, a more or less extensive reaction takes place in which the asphaltic constituents or asphalt forming constituents and oil of the crude petroleum, distillate or residuum are chemically or physically associated with the acid forming a sludge, commonly called acid sludge, which separates by gravity from and can readily be removed from the remainder of the mass. When this acid sludge is diluted with hot water or treated with steam a more or less complete separation is effected into diluted sulfuric acid and hydrocarbons and sulfonated hydrocarbons. With sludges from heavy hydrocarbons (such as paraffin oils, spindle or lubricating oils), treatment with steam effects a separation into three distinct layers, an upper oily layer, a middle layer consisting of acid tar comprising dilute sulfuric acid, hydrocarbons and sulfonated hydrocarbons, and a lower layer of diluted sulfuric acid. With acid sludges from light hydrocarbons the same separation takes place when water is added without the use of steam. With these last mentioned acid sludges little or no acid tar is formed. When cold water is used on the acid sludges from heavy hydrocarbons disintegration takes place without separation into layers, the product in such case being similar in consistency to dough, and is not, strictly speaking, an acid tar, (though when fused separation takes place into three layers, the middle one of which is acid tar) because differing therefrom physically as to structure and, it is believed, differing chemically. This dough-like product may be treated as hereinafter described, for separation of sulfonic acids or sulfonates and asphalt and oil.

It has heretofore been common practice to throw away or burn the above-mentioned acid tar which when warm is a thick fluid, but when cooled or at ordinary temperatures is often a solid, sometimes called "acid coke."

By my invention, however, I treat such acid tar, particularly when resulting from the aforementioned heavier distillate acid sludges to produce asphalt, oil, sulfonic acids or sulfonates, and emulsions.

This acid tar produced from any of the sludges as above described, consists of asphalt or asphalt forming material, oil, sulfonic acids, sulfuric acid originally used in concentrated form, sulfurous acid, water, and sulfates of organic nitrogen bases.

The acid tar or asphaltic residue from the acid sludge is first preferably though not necessarily finely divided in any way, as by granulation. Granulation may be accomplished by bringing the thick fluid mass while warm into contact with cold water and breaking up the now solid tar, as by Archimedean screw, into small particles or granules. At this stage the acid tar may be further freed of sulfuric and sulfurous acids by washing with water.

The material is emulsified by mixing with water to which there has been previously or simultaneously added, or to which there is added after mixture with the preferably finely divided or granulated material, sodium hydroxid, potassium hydroxid, lithium hydroxid, ammonia gas or ammonium hydroxid, or any other suitable hydroxid, or other suitable re-agent, such, for example, as sodium borate or carbonate, potassium borate or carbonate, ammonium carbamate, or

lithium carbonate, in quantity sufficient to neutralize the sulfuric and sulfurous acid and all or part of the sulfonic acids. The liquor is preferably simultaneously agitated, as by blowing air therethrough or by stirring to speed the action. The liquor at the beginning of this treatment is preferably relatively cool, as, for example, at 90 degrees Fahrenheit, more or less, and as the chemical re-action and emulsifying action proceed or near completion may be raised to higher temperature, as for example, 150 degrees Fahrenheit, more or less. For a charge of approximately thirty-five tons of acid coke three hours, more or less, suffice to emulsify the same.

As a result of the aforementioned reactions sodium (potassium, ammonium, lithium or other) sulfonates are formed, and these sulfonates act as emulsifying agents for those asphaltic and other compounds present. The result is an emulsion of the asphaltic and oily constituents of the acid tar, which will not break or separate at ordinary temperatures and may be used for purposes later described.

Having produced the emulsion as above described, the same is brought, in approximately three hours more for a charge of approximately thirty-five tons, to approximately 212° F. for a short time, as by injecting steam into the emulsion, the temperature of the emulsion being raised to 212 degrees Fahrenheit, more or less. If necessary water is added to thin the emulsion. When subjected to such high temperature the emulsion will break or separate. The now broken emulsion is then allowed to stand for four hours, more or less, and is kept warm until separation into layers takes place.

The emulsion then separates into two layers or masses; an aqueous lower mass or layer consisting of water, sodium or other sulfonates in solution in the water, sodium or other sulfate and sulfite in solution in the water, and some small amount of asphaltic material remaining in the emulsified state; and an oily upper layer or mass of asphalt and oil, which is readily removed and constitutes one of my products, or which may be distilled to separate from the asphalt any oil present, leaving asphalt as one of my products, the oil distillate being suitable for fuel or other purpose.

Or the emulsion of the acid tar may be agitated, as by blowing air therethrough, in the presence of benzol or other suitable solvent for the asphalt and oil, and then allowed to stand or settle with the result that there is a separation, in shorter time than in the case above described, a half hour, more or less, into two layers or masses; an aqueous lower layer or mass consisting of water, sodium or other sulfate and sulfite in solution therein, and sodium or other sulfonates in solution therein, there being practically no asphalt or oil in this layer in this case; and an oily upper layer of asphalt and oil in solution in benzol or other solvent used. This upper layer is readily removed and then distilled. The benzol or other solvent distils off and is collected and saved, and the asphalt and oil remain in the still as residuum and constitute one of my products. Or by further distillation any oil present is distilled off leaving asphalt as one of my products, the oil distillate being used for any purpose to which it is suitable, as, for example, fuel.

The liquor of the lower layers or strata separated from the emulsion by either of the modes above described may be treated as follows to separate and procure sulfonic acids or sulfonates.

This liquor may have added thereto any suitable aluminum salt, such as aluminum sulfate, which reacts with the sodium or other sulfonates present in the liquor to produce insoluble aluminum sulfonates which are precipitated, and as such may readily be separated from the liquor by filtration, decantation or other well-known methods.

Or the liquor containing the sodium or other sulfonates may have added thereto other metal salts soluble in water which react with the sodium or other sulfonates to produce insoluble sulfonates of the metal of the salt added, these insoluble sulfonates being precipitated and then readily separated from the remaining liquor by common methods.

Or the liquor containing the sodium or other sulfonates may be treated with dilute mineral acid, for example, sulfuric or hydrochloric acid, causing the precipitation of free sulfonic acids which may then readily be separated from the remaining liquor by common methods. And these recovered sulfonic acids may then be readily converted into sulfonates by causing the same to react with suitable compounds. For example, sodium sulfonates may be produced by adding to the sulfonic acids so recovered the sodium compound or salt of some weaker acid, for example, sodium carbonate; or sodium hydroxid may be added.

Or the liquor containing the sodium or other sulfonates may be evaporated to dryness or nearly so and the residue treated with alcohol or any other suitable solvent for the sodium or other sulfonates. The result is an alcoholic or other solution of such sulfonates which is readily separated from the residue consisting of sodium or other sulfates and sulfites. And this residue will contain also non-asphaltic black powder of unknown composition and the asphalt which may have remained in the emulsified condition in the lower layer or stratum resulting

from the first mentioned treatment of the emulsion. The solution of the sodium or other sulfonates in the alcohol or other solvent is then distilled, the alcohol or other solvent distilling off and is collected and saved, leaving behind as residue the sodium or other sulfonates.

The above-mentioned sulfonates and free sulfonic acids I believe are new compounds or products and they vary among themselves in composition.

The substance of dough-like consistency hereinbefore referred to as derived from cold water treatment of acid sludges of the heavier distillates may be treated as follows:

This material of dough-like consistency may be directly treated, without emulsification, with benzol or other solvent for the asphaltic material and oil in which case there results separation into two layers, an upper layer containing asphalt and oil, and a lower layer containing the bulk of the sulfonic acids and dilute sulfuric acid.

The asphaltic material and oil of the upper layer may then be separated by distilling off the solvent; and by further distillation the oil is distilled off, leaving the asphalt.

The lower layer containing the bulk of the sulfonic acids and dilute sulfuric acid may then be treated by removing the sulfuric acid and distilling off from the residue the benzol or other solvent therein leaving a residue of sulfonic acids.

The asphalt produced by any of the aforementioned modes of treatment is a new product or article of manufacture in that it more nearly resembles the natural asphalts than the artificial asphalts heretofore produced since it is much heavier and more brittle than such artificial asphalts, and is suitable, either by itself or with the oil separated therewith, for mixture with or modification of either natural asphalts or the previously known artificial asphalts derived from crude petroleum or petroleum residuum, such mixtures being suitable for roofing, paving, metal coating, etc.

The emulsions hereinbefore referred to may be caused to separate or break by subjecting the same to the action of a centrifugal machine. Or by adding alcohol, ether, benzol or some other solvent for one of the constituents of the emulsion. Or by passing electric current therethrough, whereupon finely divided matter in suspension is coagulated or comes together in masses, and so separates from the remainder of the material.

When the emulsion has been produced by employment of sodium or potassium or other borate, and particularly if the borate has been added in quantity greater than necessary to completely react with the sulfonic acids, the emulsion is a product which operates as a binder, and is an excellent binder for coal or coke in the manufacture of briquets.

For further explanation of my invention reference may be had to the accompanying drawings, in which:

Figure 1 is a diagrammatic chart of the principal features of my process.

Fig. 2 is a representation of apparatus which may be employed for treating acid tar.

The acid sludge is charged into the vessel 1 into which is delivered steam or hot water through the pipe 2 controlled by the valve 3. The application of the steam or hot water causes the disintegration into the acid tar and dilute sulfuric acid which latter is drawn off through the pipe 4 controlled by the valve 5. The acid tar is delivered through the valve 6 to the rotating Archimedean screw 7 in the trough 8 above which is disposed a pipe 9 to which water is delivered through the valve 10, the water being sprinkled from the pipe 5 upon the acid tar as it is advanced toward the right by the screw. This causes the granulation of the acid tar which is then delivered into the vessel 11 into which water is delivered from any source as pipe 10^a connecting with pipe 10. Vessel 11 communicates through the pipe 12 controlled by valve 13 with the suction of a centrifugal pump 14 which delivers the granulated acid tar in water through the pipe 15 controlled by valve 16 into the treating tank 17. Through the pipe 18 controlled by valve 19 aqueous solution of sodium hydroxid or other material hereinbefore mentioned is delivered into tank 17. The mass is then agitated by compressed air delivered through the pipe 20 which is controlled by valve 21, the pipe 20 communicating with the pipes 22 extending into the tank 17 and delivering air into the liquid and agitating the same. Through the pipes 22, or other similar pipes, steam may be delivered from time to time into the liquid mass for raising the temperature of the charge, beginning at approximately 90 degrees Fahrenheit, to approximately 150 degrees Fahrenheit. During the application of the heat and agitation an emulsion is formed as described. At this stage the operation may be discontinued and the valve 23 opened to draw the emulsion off through the pipe 24. The emulsion at these low temperatures and at lower temperatures remains as such and is suitable for use in that state, and is one of my products.

When the emulsion is not to be used as such it is raised in temperature, in the tank 17, before drawing off through valve 23, to substantially the boiling point by introduction of steam through the pipes 22. When the mass reaches such temperature the emulsion is broken or is in such state that it will

separate into layers. As soon as such temperature is reached the application of steam is discontinued. Separation now takes place into layers, the upper layer being a solution of asphaltic material in oil, and the lower layer an aqueous solution of sulfuric acid and water soluble sulfonates. While this separation is taking place the liquid is kept warm, as by introduction of slight amounts of steam from time to time, if necessary. When the separation is complete the valve 23 is opened and the lower layer of aqueous solution of acid and sulfonates drawn off through pipe 24 to the sewer, or if required for deriving sulfonic products is delivered to a suitable vessel, not shown. After the aqueous solution of the lower layer has thus been drawn off, the asphaltic material and oil are drawn off through pipe 24 to a still, not shown, where the oil may be distilled off, leaving the asphalt as residue.

What I claim is:

1. The method of producing an emulsion of asphaltic material, which consists in disintegrating acid sludge, removing the acid, neutralizing all or a part of the sulfonic acid content of the asphaltic residue in the presence of water, and agitating the mass at a temperature below emulsion breaking temperature.

2. The method of producing an emulsion of asphaltic material, which consists in treating acid sludge with steam or hot water to produce acid tar containing asphaltic material and sulfonic acids, neutralizing all or a part of the sulfonic acid content in the presence of water to form emulsifying agents consisting of water soluble sulfonates, agitating the mass, and subjecting said asphaltic material to said agents at a temperature below emulsion breaking temperature.

3. The method of producing an emulsion of material contained in acid sludge, which consists in treating acid sludge with steam or hot water, separating oil and acid, and agitating the residual acid tar in the presence of water and alkali at a temperature below emulsion breaking temperature.

4. The method of emulsifying acid tar, which consists in neutralizing all or a part of the sulfonic acid content in the presence of water to form emulsifying agents consisting of water soluble sulfonates, agitating the mass, and subjecting the same to said agents at a temperature below emulsion breaking temperature.

5. The method of emulsifying acid tar, which consists in subdividing the same, as by granulation, mixing the same with water, agitating the mass in the presence of a material reacting with sulfonic acids of the acid tar to form emulsifying agents consisting of water soluble sulfonates, and subjecting the mass to said agents at a temperature below emulsion breaking temperature.

6. The method of emulsifying acid tar, which consists in mixing the same with water, adding alkali, and agitating the mass at a temperature below emulsion breaking temperature.

7. The method of emulsifying the asphaltic component of material resulting from the treatment of petroleum or petroleum product with concentrated sulfuric acid, which consists in mixing the asphaltic material and the associated sulfonic acids in water, agitating the mass in the presence of material neutralizing the remaining sulfuric acid and reacting with the sulfonic acids to produce an emulsifying agent consisting of water soluble sulfonates, and subjecting the mass to said agent at a temperature below emulsion breaking temperature.

8. The method of emulsifying acid tar, which consists in mixing the same with water having a temperature below about 160 degrees Fahrenheit, agitating the mass in the presence of material reacting with the sulfonic acids to form an emulsifying agent consisting of water soluble sulfonates, and subjecting the mass to said agent.

9. The method of producing asphaltic material from acid tar, which consists in emulsifying the acid tar, raising the temperature of the emulsion to substantially the boiling point, allowing the emulsion to separate into layers, and recovering the asphaltic material from one of said layers.

10. The method of producing asphaltic material from acid tar, which consists in subjecting the acid tar to an aqueous solution of alkali, heating the mass to a temperature conducive to separation, allowing separation into layers, removing the asphalt and oil from one of said layers, and separating the asphalt from the oil by distillation.

11. The method of emulsifying asphaltic material or oil, which consists in subjecting the same in the presence of water to an emulsifying agent comprising water soluble sulfonates derived from acid sludge.

12. The method of deriving sulfonic acids from acid tar, which consists in emulsifying the acid tar, causing the emulsion to separate into layers one of which contains water soluble sulfonates, and treating the liquor of such layer with dilute mineral acid to precipitate free sulfonic acids.

13. The method of deriving sulfonic acids from acid tar, which consists in subjecting the acid tar to an aqueous solution of alkali, heating the mass to a temperature conducive to separation, allowing separation into layers one of which contains water soluble sulfonates, and treating the liquor containing said sulfonates with dilute mineral acid to precipitate free sulfonic acids.

14. The method of deriving sulfonates from acid tar, which consists in emulsifying the acid tar, causing the emulsion to separate

into layers one of which contains water soluble sulfonates, adding dilute mineral acid to precipitate free sulfonic acids, and treating said free sulfonic acids with a reagent to produce sulfonates.

15. The petroleum product consisting of a mixture of sulfonic acids derived from acid tar.

16. The petroleum product consisting of asphaltic material derived from acid tar.

17. The petroleum product consisting of asphaltic material derived from acid tar and substantially free of sulfonic compounds.

18. The method of emulsifying acid tar residue of acid sludge remaining after treatment of the same with hot water or steam, which consists in subjecting such residue in the presence of water through a temperature range beginning at about 90 degrees Fahrenheit and extending to about 150 degrees Fahrenheit to material reacting with the sulfonic acids to form an emulsifying agent consisting of water soluble sulfonates, and agitating the mass.

19. The petroleum product consisting of asphaltic material and oil derived from acid tar.

20. The petroleum product consisting of asphaltic material and oil derived from acid tar and substantially free of sulfonic compounds.

21. The petroleum product comprising a mixture of sulfonates derived from acid tar.

22. The product consisting of an emulsion of asphaltic material derived from acid tar.

23. The product consisting of an emulsion of asphaltic material of acid tar in water containing soluble salts of sulfonic acids of acid sludge.

24. The petroleum product consisting of asphaltic material derived from an emulsion of acid tar.

25. The method of emulsifying asphaltic material or oil, which consists in agitating the same in water containing an emulsifying agent comprising water soluble sulfonates derived from acid sludge at a temperature of substantially 90 degrees F., increasing the temperature to substantially 150 degrees F., and thereafter reducing the temperature.

26. The method of producing asphaltic material from acid sludge, which consists in subjecting the acid sludge to steam or hot water to form acid tar, emulsifying the acid tar, breaking the emulsion, and separating the asphaltic material.

27. The method of producing asphaltic material from acid sludge, which consists in disintegrating acid sludge, emulsifying a residue containing the asphaltic material, breaking the emulsion and allowing separation into layers, and separating the asphaltic material from one of said layers.

28. The method of producing asphaltic material from acid sludge, which consists in disintegrating acid sludge by subjecting the same to steam or hot water, separating the aqueous liquid and leaving a residue of acid tar containing sulfonic acids, mixing said residue with water, converting sulfonic acids into water soluble sulfonates, subjecting the asphaltic material to the emulsifying action of said sulfonates, breaking the emulsion and allowing the same to separate into layers, and separating the asphaltic material from one of said layers.

29. The method of producing asphaltic material from acid sludge, which consists in disintegrating acid sludge by subjecting the same to steam or hot water, separating the aqueous liquid and leaving a residue comprising asphaltic material, oil and sulfonic acids, converting the sulfonic acids into water soluble sulfonates, subjecting the asphaltic material and oil to the emulsifying action of said sulfonates, breaking the resulting emulsion and allowing it to separate into layers, recovering the asphaltic material and oil from one of said layers, and separating the asphalt from the oil by distillation.

30. The method of producing a water emulsion of acid tar containing sulfonic acids, which consists in mixing the same with water in the presence of a reagent producing with said sulfonic acids water soluble sulfonates.

31. The method of producing asphaltic material from acid tar containing sulfonic acids, which consists in producing a water emulsion of said acid tar by mixing the same in water in the presence of a reagent producing with the sulfonic acids water soluble sulfonates, breaking the resultant emulsion, and separating the asphaltic material.

32. The method of producing asphaltic material from acid sludge, which consists in disintegrating acid sludge, separating the aqueous liquid and leaving a residue consisting of a mixture of sulfonic acids and asphaltic material, and separating the asphaltic material from said residue.

33. The method of producing asphaltic material from acid sludge, which consists in disintegrating acid sludge, separating the aqueous liquid, emulsifying the residue, breaking the emulsion and allowing separation into layers, and recovering the asphaltic material from one of said layers.

34. The method of deriving sulfonates from acid tar, which consists in treating the acid tar with water and alkali to form an emulsion, causing the emulsion to separate into layers, and separating water soluble sulfonates from one of said layers.

35. The method of treating acid tar to produce asphaltic material and sulfonates, which consists in granulating the acid tar,

emulsifying the same by agitating the granulated acid tar in the presence of water and alkali at a temperature suitable for emulsification, breaking the emulsion and allowing the mass to separate into layers containing, respectively, asphaltic material and sulfonates in solution.

36. The method of producing asphaltic material, which consists in disintegrating acid sludge by steam or hot water, separating the resultant acid tar, subjecting the acid tar to an aqueous solution of alkali, heating the mass to a temperature conducive to separation, allowing separation into a plurality of masses, and separating the asphaltic material of one of said masses.

37. The method of producing asphaltic material, which consists in disintegrating acid sludge with steam or hot water, separating the resultant acid tar, granulating the acid tar, subjecting the acid tar granules to an aqueous solution of alkali, heating the mass to a temperature conducive to separation, allowing separation into a plurality of layers, and separating the asphaltic material of one of said layers.

In testimony whereof I have hereunto affixed my signature in the presence of the two subscribing witnesses.

RENÉ DE M. TAVEAU.

Witnesses:
H. M. NICHOLS,
F. C. ROBINSON.