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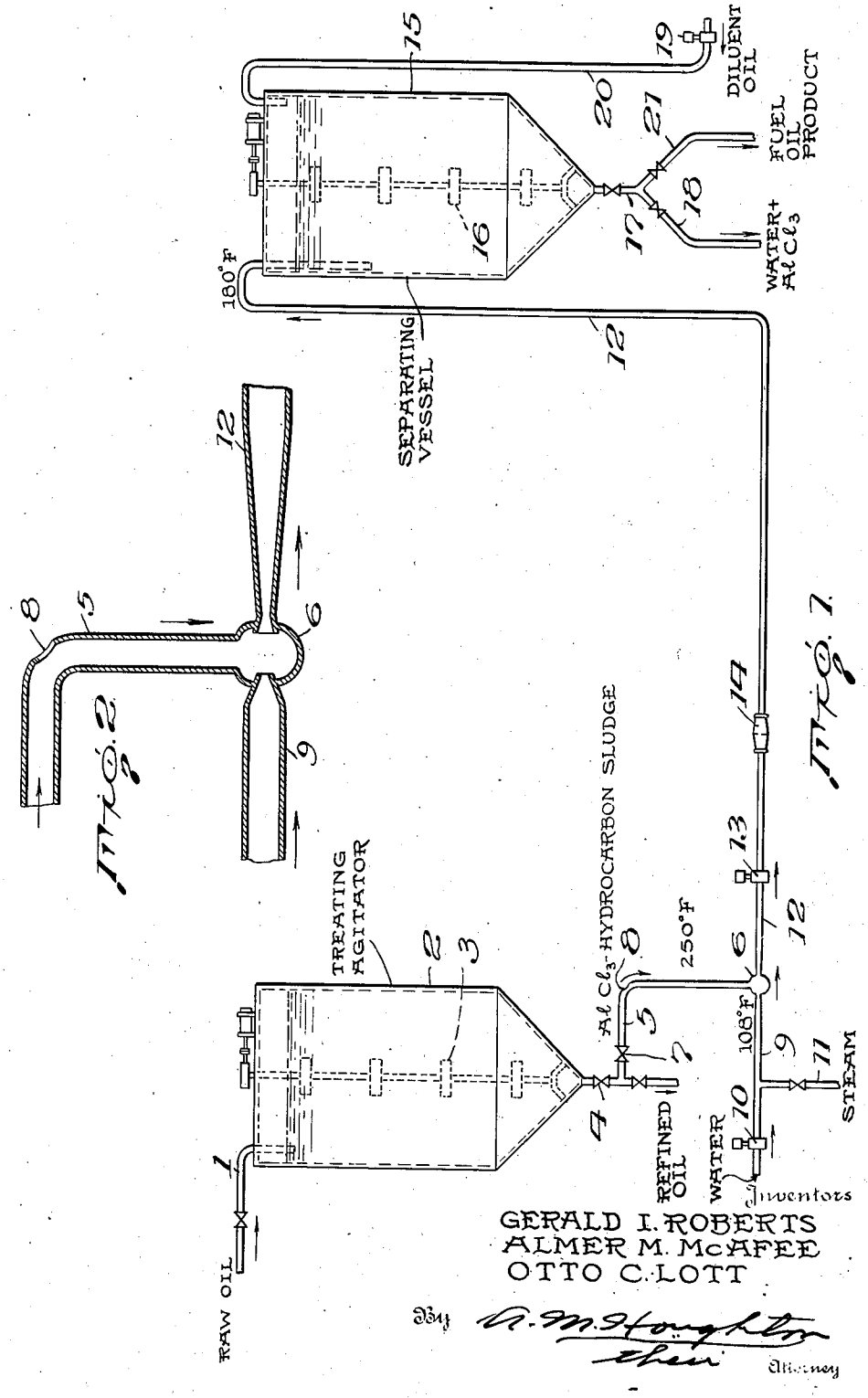

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HYDROLYSIS OF ALUMINUM CHLORIDE SLUDGE

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Our invention relates to improvements in hydrolyzing certain aluminum chloride sludges, such as result from reacting hydrocarbon oils with or in the presence of aluminum chloride at relatively low or moderately elevated temperatures.

In refining lubricating oils with anhydrous aluminum chloride, for example, the aluminum chloride reacts with undesirable hydrocarbon constituents of a lubricating oil stock to form a viscous sludge comprising mainly a mixture of double compounds of aluminum chloride and hydrocarbons, insoluble in the thereby refined oil, and having a melting point (ring and ball method) of from around 160° to around 200° F. Somewhat similar sludges also result from operations in which other types of hydrocarbon oils are reacted in the presence of aluminum chloride at low or moderately elevated temperatures, such as alkylation and condensation processes, except that the sludges derived from such process are usually of somewhat lower melting point and the hydrocarbons present therein are, in general, lower boiling than is the case with respect to residues resulting from the treatment of lubricating oils and other heavy oils with aluminum chloride.

These aluminum chloride sludges or residues having melting points not exceeding 200° F. are to be sharply distinguished from aluminum chloride residues produced in operations conducted at higher temperatures; for example, still residues produced in the distillation or cracking of hydrocarbons in the presence of aluminum chloride. In this latter type of sludge, such residues or sludges derived from high temperature alkylations have correspondingly high melting points, the hydrocarbons present having frequently undergone carbonization. They cannot easily be rendered fluid and our invention is not applicable to such sludges, although they have been successfully hydrolyzed to some extent in other ways.

The disposition and recovery of more fluid, lower-melting-point residues, to the recovery of which our invention is addressed, has for years constituted a very serious problem, especially with respect to the sludges produced in the treatment of lubricating oils. Aluminum chloride has been used as a refining agent for lubricating oils, particularly those derived from Pennsylvania crudes, to a very large extent for a number of years, so that the amounts of sludge produced are considerable.

Although it has been known for years that all aluminum chloride-hydrocarbon sludges are theoretically hydrolyzable, no satisfactory method of disposing of these sludges had been evolved prior to our invention. These sludges when cooled do not hydrolyze in cold water. Attempts have been made to hydrolyze them in tanks with hot water, but have not been successful. As soon as the temperature reaches the point where hydrolysis commences, the action is very vigorous and large quantities of hydrochloric acid fumes are evolved. From a practical standpoint it is impossible to arrest this vigorous hydrolysis once it has started. Consequently such operations have been abandoned, due to the lack of control and the serious hazards involved, due mainly to the tremendous evolution of hydrochloric acid fumes.

Prior attempts at hydrolysis of these sludges were in fact so unsuccessful and impracticable that for a number of years it has been the custom to dispose of these residues or sludges by burning them on open dumps. The hot, fluid residue leaving the oil treating vessels or agitators was run into cars and transferred to a large dump where the cars (with considerable difficulty) were unloaded, and where the burning was to take place. However, these sludges burn very slowly and with great difficulty, due to the fact that as combustion proceeds a deposit of aluminum oxide forms over the surface of the burning material. This deposit greatly interferes with combustion. As a result it takes an excessively long time for a given amount of such sludge to reach a completely burned and inactive state on a dump. In one large plant where around 1300 carloads of sludge have been dumped for burning over a long period, only about half of the material dumped thus far has been burned. It is necessary to rake over the dump heap at frequent intervals to facilitate combustion, and during damp or rainy weather tremendous quantities of acid fumes are evolved.

It can readily be seen that an operation of this character is expensive and wasteful and constitutes a serious nuisance Such a method of disposal would never have been adopted or used had any successful method of hydrolysis been available.

Our present invention has made it possible to overcome the disadvantages and difficulties of prior methods of disposing of aluminum chloride sludges of the character indicated and, furthermore, has made it possible to recover the hydrocarbons present in such sludges in the form of a valuable product, i. e., as a heavy but not too

viscous oil sufficiently low in ash and acid content to constitute a useful fuel. This is accomplished in accordance with our present invention with considerable ease and at a low cost.

In accordance with our present invention, an aluminum chloride sludge of the character indicated, that is to say, a sludge having a melting point of not more than about 200° F., regardless of source, is withdrawn from the contacting vessel while still in a hot and fluid condition and is induced or delivered into a flowing stream of water at a controlled temperature and in relatively large quantity. The flowing stream of water containing the added sludge is then passed through a pipe sufficiently long to permit substantial completion of hydrolysis within the pipe, and is delivered to a collecting vessel, where separation occurs. The water containing small amounts of dissolved aluminum chloride is withdrawn, preferably at a rate corresponding to the rate of its introduction into the separating vessel, while the liberated hydrocarbons remain in the separating vessel. After the sludge has all been withdrawn from the original contacting vessel, hydrolyzed and transferred into the separating vessel, the flow of water is terminated and all water is removed from the separating vessel. A diluent oil is then introduced into the separating vessel, where it is agitated with the hydrocarbons liberated from the sludge until a condition of substantial homogeneity has been reached. The resultant fuel oil is then withdrawn from the separating vessel for use as desired.

We have found that if the diluent oil is added to the separating vessel either before or during the time of transfer of the sludge thereto, emulsion troubles are likely to be encountered in most cases. Therefore, the diluent oil is not added to the separating vessel until the entire hydrolyzing and transferring operation has been completed and the water has been withdrawn from the latter as completely as possible. Enough diluent, of a sufficiently fluid character, is then added to reduce the viscosity of the final fuel oil product to a suitable point or to reduce the ash content of the final diluted oil to whatever point is desired or both. It is also important to dilute the liberated hydrocarbons sufficiently to permit separation from any residual water which may remain therein after the primary water separation stage.

The amount of water required is considerably in excess of that of the sludge and is governed largely by the character and temperature of the sludge. Enough water is added, at a sufficiently high temperature, not merely to supply that theoretically necessary for hydrolysis but also to control the temperature and to insure that hydrolysis will be substantially completed before the flowing stream reaches the separating vessel, so that liberation of acid fumes from the separating vessel may be avoided. Ordinarily we employed from 3 to 7 parts by volume of water for each part by volume of sludge, and the water is introduced to the sludge at a temperature of from 100° to 125° F. (the sludge being at 225° to 270° F.), in order to maintain a temperature of from 150° to 200° F. at the point where the resultant stream of water and sludge reaches the separating vessel.

The manner of mixing is important. While vaious types of apparatus may perhaps be employed, we have secured exceptionally satisfactory results by using a mixing nozzle of the type commonly used for mixing foam-producing chemicals with water for the purpose of making fire-extinguishing foams. Such a nozzle, frequently referred to as an ejector, is provided with a central chamber having a side inlet through which the sludge may be introduced. A stream of water enters the central chamber through a more or less restricted nozzle at right angles to the entering flow of sludge, and the combined flow of water and sludge passes out through a second nozzle of Venturi type. Such a nozzle is ideally suited for the purposes of our invention.

In order that our invention may be more fully set forth and understood, we now describe, with reference to the drawing accompanying and forming part of this specification, a preferred manner in which it may be practiced and embodied. In the drawing,

Fig. 1 is a more or less diagrammatic elevational view of an apparatus for treating hydrocarbon lubricating oil stock with anhydrous aluminum chloride and for effecting hydrolysis and recovery of the sludge thereby produced; and

Fig. 2 is a vertical sectional view of a form of nozzle also illustrated in Fig. 1 and useful in the performance of our invention.

Similar reference numerals designate similar parts in both views of the drawing.

Referring now to the drawing, and more particularly Fig. 1 thereof, raw lubricating oil stock to be refined is introduced through a valve line 1 to a treating vessel 2, of conventional type. The vessel 2 is provided with an agitating device 3 of suitable type.

After a suitable quantity of oil has been introduced into the vessel 2, aluminum chloride is added and the oil and aluminum chloride are agitated together. A vigorous reaction takes place, the aluminum chloride reacting with undesirable constituents of the stock (mainly of an unsaturated, naphthenic or aromatic character) resulting in the formation of a double compound of aluminum chloride and the reacted constituents; this sludge is insoluble in the refined paraffinic oil and may readily be separated therefrom at the temperatures which obtain at the end of the treatment. These are usually in excess of 225° F. A typical sludge produced in an operation of this kind, in which Pennsylvania lubricating stock is refined with aluminum chloride, has a melting point of from about 160° to about 190° F., and subsists at a temperature of about 250° F. at the completion of the refining operation.

After the reaction has been completed agitation is stopped and separation occurs. A valve 4 at the bottom of the agitator is then opened and the sludge is then withdrawn through a valved line 5 into a mixing nozzle 6, the details of which are more fully illustrated in Fig. 2. In addition to a valve 7, the line 5 is preferably provided with an orifice or sight-hole 8, whereby the flow of sludge through the line 5 may be observed and controlled.

Water is introduced to the nozzle 6 through a line 9, which may be provided with a pump 10, and where necessary, steam is also supplied to the line 9 through a valved inlet 11 in sufficient quantity to bring the temperature of the water entering the mixing nozzle 6 to the desired point. In a typical instance we have employed 5 parts by volume of water and condensed steam, at a temperature of about 108° F., for each part of aluminum chloride sludge leaving the treating vessel 2 at a temperature of about 250° F.

The mixture of water and sludge leaving the nozzle 6 then passes through a line 12 wherein is located a pump 13, preferably of a centrifugal type, and wherein may also be located a mixing device 14 of more or less conventional type. The line 12 is made long enough to insure that hydrolysis of the sludge will be complete or substantially complete by the time the mixture reaches the end of the line, as is indicated by minimum evolution of hydrochloric acid fumes at the discharge point.

After passing through the line 12, the mixture of oil and sludge, in which hydrolysis has now taken place, enters a separating vessel 15. As shown in the drawing, this vessel 15 may be substantially similar in construction to the treating vessel 2, and is also provided with agitating means 16 of conventional type. Under ordinary circumstances, however, little or no agitation is provided during the time of transfer of sludge into the vessel 15, for it is found that separation takes place immediately. The liberated hydrocarbons separate into an upper layer, while the water (containing liberated and dissolved aluminum chloride) settles to the bottom of the vessel and is withdrawn through a line 17 and a valved branch line 18. In a typical instance, the water thus withdrawn has a pH value of about 2.5 and can be discarded without difficulty.

After all the sludge has been transferred from the agitator 2 into the vessel 15, the flow of water and steam is shut off, and the remaining water is withdrawn as far as possible from the bottom of the vessel 15. The valved line 18 is then closed and diluent oil is introduced by means of a pump 19 and a line 20 into the separating vessel 15. Various quantities and types of hydrocarbon oils may be used for diluting purposes, depending upon the desired characteristics of the final fuel product. Ordinarily, however, we have found that the addition of one barrel of solar oil per three barrels of liberated hydrocarbons from the sludge gives satisfactory results.

After addition of the diluent oil, the mixture of liberated hydrocarbons and diluent is agitated for a brief period to insure thorough mixing as well as separation of any small quantities of water which may remain. Such water, when necessary, is removed through the valved line 18, after which the fuel oil product is removed through a valved branch line 21 and transferred to storage or to fuel burners.

In a typical instance in which one part by weight of solar oil was added per 5 parts by weight of liberated hydrocarbon tar, there was produced a fuel oil having the following characteristics:

Gravity	13.7° API
Viscosity (furol)	54 seconds at 122° F.
Flash	230° F.
Pour point	0° F.
Water and sediment	15%
Sediment by extraction	11.7%
Carbon residue	13.39%
Ash	0.38%
Acid—about	0.0003%

Such a product may be burned without difficulty in fuel burners of the ordinary type commonly used in boiler houses and the like. It will be obvious, however, that products of varying degrees of viscosity and of varying ash content and the like may readily be obtained by judicious blending with proper diluents. Some dilution is almost always necessary, however, on account of the high viscosity and high melting point of the released hydrocarbons, when in undiluted form.

While we have described our invention hereinabove with respect to various operating details, it will be readily understood by those skilled in the art that our invention is not limited to such details but may be variously practiced and embodied within the scope of the claims hereinafter made.

What we claim is:

1. In the treatment and disposal of aluminum chloride-hydrocarbon sludges which melt at temperatures of not more than about 200° F. and are produced in treating hydrocarbons with aluminum chloride at relatively low temperatures, the improvement which comprises introducing said sludge in a hot fluid condition into an enclosed flowing stream of water, passing the resulting mixture of sludge and water through an enclosed conduit of sufficient length and at such a rate that hydrolysis of the aluminum chloride is substantially complete when the mixture reaches the exit end of said conduit, delivering the thus hydrolyzed aluminum chloride, sludge and water to a vessel adapted to settle the mixture and form an oily and an aqueous layer, and separately removing said aqueous and oily layers.

2. In the treatment and disposal of aluminum chloride sludges which melt at temperatures of not more than about 200° F. and are formed in relatively low temperature refining processes involving the treatment of petroleum oils with aluminum chloride, the improvement which comprises withdrawing said sludge from the refining operation while it is still in a hot fluid condition and introducing the hot fluid into an enclosed flowing stream of water, passing the resulting mixture of sludge and water through an enclosed conduit of sufficient length and at such a rate that hydrolysis of the aluminum chloride is substantially complete when the mixture reaches the exit end of said conduit, delivering the thus hydrolyzed aluminum chloride, sludge and water to a vessel adapted to settle the mixture and form an oily and an aqueous layer, and separately removing said aqueous and oily layers.

3. In the treatment and disposal of aluminum chloride sludges which melt at temperatures of not more than about 200° F. and are formed in relatively low temperature refining processes involving treatment of petroleum oils with aluminum chloride, the improvement which comprises withdrawing said sludge from the refining operation while it is still in a hot fluid condition and introducing the hot fluid into an enclosed flowing stream of water, passing the resulting mixture of sludge and water through an enclosed conduit and regulating the temperature of the water, rate of flow and length of the conduit such that the hydrolysis of the aluminum chloride is substantially complete when the mixture reaches the exit end of said conduit, delivering the thus hydrolyzed aluminum chloride, sludge and water to a vessel adapted to settle and separate the mixture into an oily and an aqueous layer, and separately removing said aqueous and oily layers.

4. In the treatment and disposal of aluminum chloride sludges which melt at temperatures of not more than about 200° F. and are formed in relatively low temperature refining processes in-

volving treatment of petroleum oils with aluminum chloride, the improvement which comprises withdrawing said sludge from the refining operation while it is still in a hot fluid condition and introducing the hot fluid into an enclosed flowing stream of water, passing the resulting mixture of sludge and water through an enclosed conduit and regulating the temperature of the water, the rate of flow and length of the conduit such that the hydrolysis of the aluminum chloride is substantially complete when the mixture reaches the exit end of said conduit, delivering the thus hydrolyzed aluminum chloride, sludge and water to a vessel adapted to settle and separate the mixture into an oily and an aqueous layer, removing the aqueous layer from said vessel, diluting the remaining oily layer with an oil, and withdrawing the resulting oily mixture from said vessel.

5. In the treatment and disposal of aluminum chloride sludges which melt at temperatures of not more than about 200° F. and are formed in relatively low temperature refining processes involving treatment of petroleum oils with aluminum chloride, the improvement which comprises withdrawing said sludge from the refining operation while it is still in a hot fluid condition, introducing the hot fluid into a pipe connected with a chamber, exerting suction on said fluid in said pipe and causing it to mix with water in said chamber by means of a stream of water flowing through a nozzle at right angles to said pipe into said chamber and out of said chamber through a Venturi nozzle at right angles to said pipe, passing the stream of sludge and water thus formed through an enclosed conduit, regulating the temperature of the water, the rate of flow and the length of the conduit such that the hydrolysis of the aluminum chloride is substantially complete when the mixture reaches the exit end of said conduit, delivering the thus hydrolyzed aluminum chloride, sludge and water to a vessel adapted to settle and separate the mixture into an oily and an aqueous layer, and separately removing said aqueous and oily layers.

6. In the treatment and disposal of aluminum chloride sludges which melt at temperatures of not more than about 200° F. and are formed in relatively low temperature refining of lubricating oil stock with aluminum chloride, the improvement which comprises withdrawing said sludge from the refining operation while it is still in a hot fluid condition and introducing the hot fluid into an enclosed flowing stream of water, passing the resulting mixture of sludge and water through an enclosed conduit, regulating the temperature of the water, the length of the conduit and the rate of flow such that hydrolysis of the aluminum chloride is substantially complete when the mixture reaches the exit end of said conduit, delivering the thus hydrolyzed aluminum chloride, sludge and water to a vessel adapted to settle and separate the mixture into an oily and an aqueous layer, and separately removing said aqueous and oily layers.

7. In the treatment and disposal of aluminum chloride sludges which melt at temperatures of not more than about 200° F. and are formed in relatively low temperature refining of lubricating oil stock with aluminum chloride, the improvement which comprises withdrawing said sludge from the refining operation at a temperature of from about 225° to about 275° F., continuously mixing said sludge in an enclosed space and while in a hot fluid condition with from about 3 to about 7 times its volume of water maintained at a feed temperature of from about 100° to about 125° F., passing the resulting mixture through an enclosed conduit and regulating conditions of flow and length of the conduit such that at the exit end of said conduit the hydrolysis of the aluminum chloride is substantially complete and the temperature of the mixture lies between about 150° and about 200° F., delivering the resulting mixture to a vessel adapted to separate it into oily and aqueous layers, removing the aqueous layer, diluting the oily layer with an oil and withdrawing the resulting oily mixture.

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