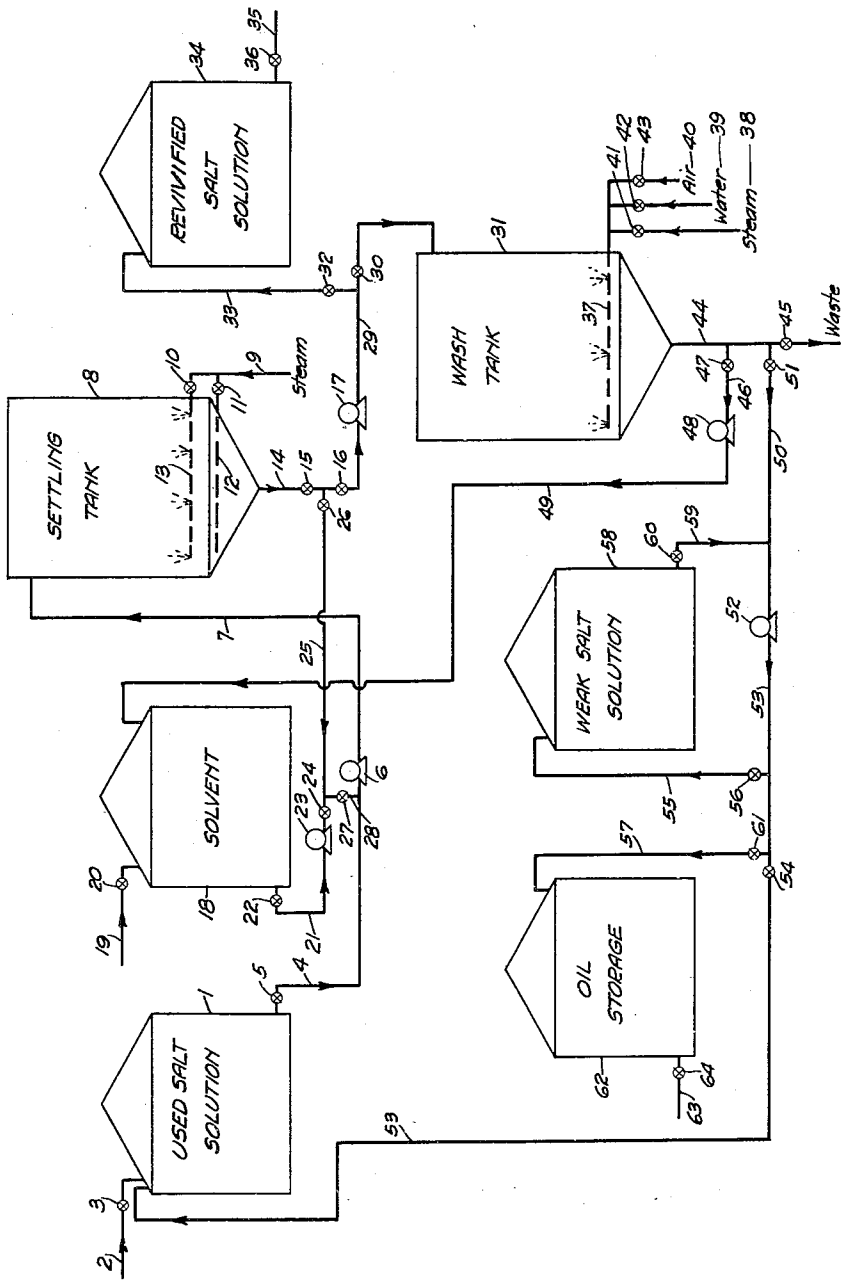
July 17, 1934. J. H. LOOMIS ET AL 1,966,729

PROCESS OF TREATING METALLIC SALT SOLUTIONS

Filed Aug. 28, 1933



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Patented July 17, 1934

1,966,729

UNITED STATES PATENT OFFICE

1,966,729

PROCESS OF TREATING METALLIC SALT SOLUTIONS

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Application August 28, 1933, Serial No. 687,160

8 Claims. (Cl. 23—50)

This invention relates to revivification of metallic salt solutions associated with impurities, which have been used in purifying and refining hydrocarbon oil by contact therewith, and is especially adapted for revivifying such salt solutions after use as described in U. S. Patent #1,809,170, issued to Arthur Lachman June 9, 1931, Process of refining hydrocarbon oils, which describes the purification and refining of hydrocarbon oils in vapor phase, using water solutions of metallic salts or mixtures thereof, such as the chloride, bromide, iodide, sulphate, nitrate, etc., of zinc, copper, cadmium, mercury, iron, chromium, manganese, aluminum, nickel and cobalt.

In general, this invention may be used to revivify for reuse any of the metal salt solutions which have been used for purifying and refining hydrocarbon oils by any known method, and which may also include, in addition to the above named salts, salts of magnesium, calcium, ammonia, oxychlorides, mixed base oxyhalides and double salts.

Metal salts dissolved in water, when used to refine hydrocarbon oil such as gasoline, naphtha, or other like hydrocarbon oil distillates, take up impurities, notably oil coloring matter, which may be nitrogen base compounds and other organic oils, or oil compounds of unknown chemical composition, until they are rendered more or less inert by the inhibiting action of the adsorbed oils or constituents, which may be in part in chemical combination therewith.

In the use of water solutions of metallic salts, such, for example, as concentrated solutions of zinc chloride, for purifying and stabilizing gasoline stock or other distillates by contact therewith, we have discovered that the compounds which gradually render inert the zinc chloride in use are composed largely of nitrogen bases such as pyridines and resinous compounds, particularly when gasoline stocks derived from cracked petroleum oil products are treated. We believe that the resinous compounds are produced during the treatment of gasoline stock with the metallic salts by polymerization of acetylene and diolefine hydrocarbons contained in the stock, while the nitrogen base compounds are usually produced in the cracking of petroleum oil containing fixed nitrogen.

The amount of impurities contained in a metal salt solution, such as a water solution of zinc chloride having a concentration of, say, 70 to 85 per cent, after having been used for a period of time to refine cracked gasoline stock by the liquid or vapor phase method at temperatures of approximately 300 to 340° F. or higher, may amount to as much as 23 per cent by volume of the zinc chloride solution.

Now we have discovered that if these metal salt solutions be treated after use with a solvent of the impurities, such as benzol, toluol, xylol, phenol, cresylic acid, resorcinol, hydroquinone, nitrobenzene, monochlorbenzene, benzyl alcohol, or other like solvent compounds of the benzol type or carbocyclic series, which may be compounds containing one or more hydroxyl, nitro or haloid groups, or mixtures thereof, the impurities contained therein may be separated and the metal salt solution revivified. Furthermore, we have determined that the extracted impurities can be recovered from the solvent in commercially valuable form.

An object of this invention is to revivify metal salt solutions which have been used to purify and refine hydrocarbon oil, so that the revivified metal salt solutions may be continuously used for the further purification and refining of hydrocarbon oils.

Another object of the invention is to revivify metal salt solutions, which have been used to purify and refine hydrocarbon oils, with solvents, whereby the original active power of the salt solutions may be restored, and the separated impurities recovered in commercially valuable form.

We have further found that the restoring of the active powers of the salt solutions, the recovery of the impurities in commercially valuable form, and the recovery of the solvent employed in the process for reuse, may be most economically conducted in apparatus which will be herein described. Reference is therefore made to the following drawing, which illustrates diagrammatically the preferred apparatus in which the process may be conducted.

In the drawing, 1 represents generally a tank for holding the salt solution to be revivified. Pipe 2, controlled by valve 3, connects tank 1 to a source of used salt solution to be treated. Pipe 4, controlled by valve 5, connects used salt solution tank 1 near the bottom to the inlet of pump 6. Pipe 7 connects the discharge of pump 6 to settling tank 8 near the top. A suitable closed steam heating pipe or coil 12, and an open steam spray pipe 13 are provided within settling tank 8, and are connected to a source of steam through steam pipe 9, controlled by valves 10 and 11. Pipe 14, controlled by valves 15 and 16, connects settling tank 8 at the bottom to the inlet of pump 17.

Tank 18, stationed at any convenient place, is provided to hold the liquid solvent used in the process. Pipe 19, controlled by valve 20, connects solvent tank 18 near the top to a source of solvent supply. Pipe 21, controlled by valve 22, connects solvent tank 18 near the bottom to the inlet of pump 23. Pipe 25, controlled by valves 24 and 26, connects the discharge of

pump 23 to pipe 14. A branch pipe 28, controlled by valve 27, connects pipe 25 to pipe 4.

Pipe 29, controlled by valve 30, connects the discharge of pump 17 to wash tank 31 near the top. Pipe 33, controlled by valve 32, connects pipe 29 to revivified salt solution tank 34 near the top. Pipe 35, controlled by valve 36, connects revivified salt solution tank 34 near the bottom to other storage or to a treater not shown. A suitable spray pipe 37 is provided within wash tank 31, which is connected to separate sources of water, steam and air through branch pipes 38, 39 and 40, controlled by valves 41, 42 and 43. Pipe 44, controlled by valve 45, connects wash tank 31 at the bottom to a waste disposal.

Pipe 46, controlled by valve 47, connects pipe 44 to the inlet of pump 48. Pipe 49 connects the discharge side of pump 48 to solvent tank 18 near the top. Pipe 50, controlled by valve 51, connects pipe 44 to the inlet of pump 52. Pipe 53, controlled by valve 54, connects the discharge of pump 52 to used salt solution tank 1 near the top. Pipe 55, controlled by valve 56, connects pipe 53 to weak salt solution tank 58 near the top. Pipe 59, controlled by valve 60, connects weak salt solution tank 58 near the bottom to pipe 50. Pipe 57, controlled by valve 61, connects pipe 53 to oil storage tank 62 near the top. Pipe 63, controlled by valve 64, connects oil storage tank 62 near the bottom to other storage not shown, or place of use therefor.

The preferred process as carried out in the apparatus just described is as follows:

A water solution of metallic salt or salts, such as a substantially concentrated solution of zinc chloride or other salts, which has been used for purifying hydrocarbon oils and contains impurities such as heretofore described, contained in tank 1, is caused to flow through pipe 4 and into the inlet of pump 6, the rate of flow being controlled by operation of valve 5. At the same time a regulated flow of the treating solution, contained in solvent tank 18, is caused to flow through pipe 21, controlled by valve 22, and into the inlet side of pump 23. Pump 23 discharges the solvent in stream flow at the required rate into pipe 25, from where it passes through branch pipe 28 and into pipe 4, valves 24 and 27 being open and valve 26 closed. In pipe 4 the solvent and used salt solution coming from tank 1 are mixed, and are thoroughly commingled in pump 6, which discharges the commingled mixture through pipe 7 into settling tank 8.

The quantity of solvent required to revivify the used salt solution may vary through a wide range, depending upon the amount and characteristics of the impurities contained in the used salt solution. In general practice we have found that ten parts of the used salt solution usually required about one part of solvent, such as commercial creosote, crude carbolic acid, chlorinated hydrocarbons of the benzol type or series, or phenols dissolved in hydrocarbons of the benzol type or series, although used salt solutions in some cases may be revivified using as little as one-half part or less, while in other cases as much as five parts or more of solvent may be required. While hydrocarbons of the benzol type or series may be used alone as the solvent, preferably about 15 per cent or more of a phenol is added to the hydrocarbon, although pure phenol alone may be used.

Tank 8 is filled to any desired level with the commingled salt solution containing the required amount of solvent, which may be therein heated to any desired temperature, of say 100 to 150° F., to facilitate the separation of the solvent and dissolved impurities from the treated salt solution. This may be carried out by opening valve 11, thereby permitting steam to pass through pipe 12 from pipe 9, which is connected to a source of steam, or by opening valve 10 in spray pipe 13, which is also connected to steam pipe 9.

By the introduction of open steam into the commingled mixture of salt solution and solvent, the mixture may be agitated, heated, and the concentration of the salt solution reduced to any required degree; or the mixture of salt solution and solvent may be agitated and maintained in a mixed state for any length of time required by circulating same from the bottom of settling tank 8 through pipes 14, 25, 28, pump 6, and pipe 7, which is connected to tank 8 near the top, by operating pump 6 with valves 15, 26 and 27 open and valves 24, 16 and 5 closed.

After the salt solution has been maintained in contact with the solvent for the required length of time, valves 15, 26 and 27 are closed and the commingled mixture is permitted to stand quiescent until the solvent containing the dissolved impurities separates from the treated salt solution, forming a top layer when concentrated solutions of salts, such as the chlorides, having a greater specific gravity than the solvent, are revivified. When dilute water solutions of salts are revivified with a solvent having a specific gravity greater than the salt solution, the salt solution will form the top layer and the solvent containing the dissolved impurities the bottom layer.

After separation of the solvent containing the dissolved impurities from the treated salt solution in settling tank 8, the revivified treated salt solution is withdrawn into revivified salt solution tank 34, passing from the bottom of tank 8 through pipe 14 and into the inlet of pump 17, valves 15 and 16 being open and valve 26 closed. Pump 17 discharges the revivified salt solution through pipes 29 and 33 into revivified salt solution tank 34, valve 32 being open and valve 30 closed. From tank 34 the revivified salt solution may be conveyed to other storage through pipe 35, controlled by valve 36, and may be thereafter again used for purifying and refining hydrocarbon oil, either with or without a further concentration thereof.

After withdrawal of the revivified salt solution, the separated solvent containing the dissolved impurities is conveyed from tank 8 into wash tank 31 through pipe 14, pump 17 and pipe 29, by opening valves 15, 16 and 30 and operating pump 17, valves 32 and 26 being closed. In wash tank 31 the extracted impurities contained by the solvent are separated by washing with water, preferably hot water maintained at a temperature below the vaporizing temperature of the solvent, such, for example, as 100 to 150° F. when benzol comprises a portion of the solvent. This operation is preferably carried out by the introduction of water and steam into tank 31 through pipes 38 and 39, which are connected to spray pipe 37, the flow from each being controlled by operation of valves 41 and 42 respectively. After the required quantity of hot water has been introduced into tank 31, the liquid contained there-

in is agitated with air by opening valve 43 in air pipe 40, which is also connected to spray pipe 37.

After the hot water and used solvent have been commingled or contacted for a sufficient period of time to decompose and dissolve the salt compounds contained therein, valve 43 is closed and the commingled mixture is permitted to stand quiescent until separation takes place in three layers, the top layer being a colored oil which may be composed principally of polymerized products and nitrogen base oils, or may be colored oils or compounds of unknown composition. The middle layer consists principally of the solvent, which may contain certain small amounts of the extracted impurities of unknown composition. The bottom layer consists of a dilute water solution of the salt, which may contain small percentages of the extracted impurities.

The separated dilute water solution of the salt is transferred from wash tank 31 through pipes 44, 50, 53 and 55 into weak solution tank 58 by operation of pump 52, with valves 51 and 56 open and valves 47, 45, 54, 60 and 61 closed. The weak salt solution containing impurities, thus recovered in tank 58, may be returned to tank 1 through pipes 59, 50 and 53 by operating pump 52 with valves 60 and 54 open and valves 51, 56 and 61 closed, and reprocessed along with other salt solutions to be revivified; or the weak salt solution may be concentrated before it is returned to tank 1; or in some cases it may be used after concentration without further treatment.

The recovered solvent and the colored oil, after removal of the weak salt solution, may be given water washes to further free them of water soluble compounds, the wash water separated, after which they are separately transferred into their respective tanks 18 and 62, the recovered solvent passing from said tank 31 through pipes 44, 46 and 49, controlled by operation of pump 48 with valve 47 open and valves 45 and 51 closed. The colored oil in tank 31, after removal of the solvent, passes through pipes 44, 50, 53 and 57 by operation of pump 52, with valves 51 and 61 open and valves 54, 56, 60, 45 and 47 closed. The solvent thus recovered and transferred into tank 18 may be continuously used for the further revivification of used salt solutions, with the occasional addition of new solvent to make up for losses incurred in the recovery operation. The colored oil products recovered may be used, either alone or in combination with other oils, for the production of spray oil for the extermination of injurious pests, such as insects, vermin or the like, or for other purposes known in the art.

Prior to the revivification operation, in certain cases, when the used metallic salt solution contains relatively large percentages of oxy-salts or oxy-compounds and sulphides, it may be treated with a water solution of a mineral acid in amounts sufficient to convert such compounds into the corresponding salt.

While the process herein described is well adapted for carrying out the objects of the present invention, it is to be understood that various modifications and changes may be made without departing from the spirit of the invention, and the invention includes all such modifications and changes as come within the scope of the appended claims.

We claim:

1. A process of revivifying a water solution of metallic salt containing extracted constituents resulting from oil refining processes, comprising, commingling the salt solution with a solvent of the constituents which is insoluble in the salt solution, and then separating the solvent and dissolved constituents from the salt solution.

2. A process of revivifying a water solution of metallic salt containing extracted constituents resulting from oil refining processes, comprising, commingling the salt solution with a solvent of the constituents consisting of hydrocarbons of the benzol type, and then separating the solvent and dissolved constituents from the salt solution.

3. A process of revivifying a water solution of metallic salt containing extracted constituents resulting from oil refining processes, comprising, commingling the salt solution with a solvent of the constituents consisting of substituted hydrocarbons of the benzol type, and then separating the solvent and dissolved constituents from the salt solution.

4. A process of revivifying a water solution of metallic salt containing extracted constituents resulting from oil refining processes, comprising, commingling the salt solution with a solvent of the constituents consisting of hydrocarbons of the benzol type containing substituted hydrocarbons of the benzol type, and then separating the solvent and dissolved constituents from the salt solution.

5. A process of revivifying a water solution of metallic salt containing extracted constituents resulting from oil refining processes, comprising, commingling the metallic salt solution with a solvent of the constituents consisting of hydrocarbons of the benzol type containing a phenol, and then separating the solvent and dissolved constituents from the salt solution.

6. A process of revivifying a water solution of metallic salt containing extracted constituents resulting from oil refining processes, comprising, commingling the salt solution with a solvent of the constituents consisting of hydrocarbons of the benzol type containing a substituted inorganic acid radical, and then separating the solvent and dissolved constituents from the salt solution.

7. A process of treating a water solution of metallic salt containing extracted constituents resulting from oil refining processes, comprising, commingling the metallic salt solution with a solvent of the constituents which is insoluble in the salt solution, then separating the solvent and dissolved constituents from the salt solution, and finally separating the said dissolved constituents from the solvent by washing with water.

8. A process of revivifying a water solution of metallic salt containing extracted constituents resulting from oil refining processes, comprising, treating the salt solution with a mineral acid, and then with a solvent of the constituents which is insoluble in the salt solution, then separating the solvent and dissolved constituents from the salt solution.

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