Patented May 22, 1945 2,376,644

# UNITED STATES PATENT OFFICE

2,376,644

## PROCESS OF TREATING LIGHT OILS PRODUCED IN BY-PRODUCT COKING OF BITUMINOUS COAL IN ORDER TO OBTAIN A WATER-SOLUBLE ACID SLUDGE

Joseph H. Wells and Philip J. Wilson, Jr., Pittsburgh, Pa., assignors to Carnegie-Illinois Steel Corporation, a corporation of New Jersey

No Drawing. Application January 2, 1943, Serial No. 471,212

8 Claims. (Cl. 196—31)

In by-product coke works, a considerable problem arises in the disposal of acid sludge which results from the washing of light oils. The disposal of such material without contaminating the atmosphere or polluting a stream, or otherwise creating a menace to public health, constitutes a large and difficult problem.

The light oil which is recovered from the gas produced in a by-product coke plant consists principally of benzene, toluene, and xylene. Many other compounds are present in less amounts and they must be separated from the benzene and its homologs in order to obtain a marketable benzene and the like.

An important group of such compounds which must be thus removed are sulphur-containing organic compounds, of which group carbon disulphide and thiophene are representative compounds.

Another group of compounds which must be removed includes unsaturated compounds including dienes and olefins. Pentenes, cyclopentadiene, styrene, and indene are representative of this group.

Still other classes of compounds are present as well, but the sulphur-containing compounds and the unsaturated compounds are the two most important impurities. Although some of these compounds are separated for sale, with respect to the pure benzene and its homologs, they must be considered as impurities.

Of the impurities, one to two per cent, based on the volume of the light oil, distill below 80° C., the boiling point of benzene. A large proportion of these forerunnings can be separated from the bulk of the light oil by fractional distillation. In this fraction of the light oil are found cyclopentadiene and carbon disulphide.

Another portion of the light oil distills above 145° C. the boiling point of ortho-xylene, and likewise can be separated to a large extent by fractional distillation. In this fraction will be found cumarone, mesitylene, indene, and naphthalene.

The forerunnings and the high-boiling fraction of the light oil do not include all of the impurities; a certain proportion distills between 80° C. and 145° C. The impurities boiling in this temperature range cannot be separated by fractional distillation, but can be removed by treating the light oil with sulphuric acid. The acid reacts with the impurities in different ways. Some compounds it will polymerize to high molecular resins or pitches; others will sulphonate; and still others are oxidized. The reactions are extremely complex, and little is known of them. The acid also will react in a similar manner with any forerunnings or high-boiling compounds which may be left in the fraction to be washed.

In the commercial refining of light oil, the oil is first fractionated crudely to take out the highest boiling compounds. In some cases this fractionation may include removal of forerunnings boiling below 80° C.

The distilled light oil then is washed with concentrated sulphuric acid in a large vertical, cylindrical tank equipped with a mixing device. Several per cent by volume of the acid are run into the oil in the mixing tank or agitator. The two are mixed at substantially room temperature until the reaction between acid and impurities has proceeded sufficiently far to insure their removal from the oil. On settling, a heavy layer, which consists of unused acid and complex products of the reaction, collects in the bottom of the agitator. This layer is sticky and viscous with a brownish-red or purple color and a strong odor of sulphur dioxide.

This acid sludge is difficult of disposal. For one reason, its high acid content renders it corrosive to equipment in which it is handled. If the sludge is burned, the sulphur from its organic matter and excess acid is evolved as sulphur dioxide and sulphur trioxide which may pollute the atmosphere very seriously. If thrown on a dump the high content of organic matter makes the sludge a fire hazard. In addition, the dump must be fenced off carefully so that human beings and animals will be unable to get into it by accident.

A great deal of study has been devoted to finding some process which will improve the quality of this sludge, a better method for its disposal, or some use for it. The sludge still contains a large proportion of the original sulphuric acid which has not reacted. Several methods are used for recovery of this acid.

One of these methods is to boil the sludge with steam. During the boiling, the sludge separates into two layers, one a mass of pitch and the other dilute, but impure acid. The latter usually can be used around the plant, but the disposal of the pitch still is a problem. This process does have the advantage, however, that the volume of the sludge to be disposed of is reduced.

Another method for recovery of the acid is to dilute the acid layer in the agitators after the washing of the oil has been completed. After the oil and concentrated acid have been agitated together for the proper time, water is added and

agitation is continued. When the acid phase and the water have been properly contacted, the agitator is stopped, and the contents of the vessel are allowed to settle. Three separate layers form in the agitator. At the bottom is a layer of diluted acid, relatively low in organic matter, which acid is referred to as spent acid. Above this is a viscous layer of polymerized and reacted organic matter which still contains some acid and some oil, possibly both in solution and entrained. In the subsequent discussion, this will be termed the acid sludge. On top is the washed light oil.

The acid sludge and spent acid are drawn off together from the agitator into a lead-lined tank and there are boiled with direct steam. The steam vaporizes any light oil present, and the latter distills off and is condensed. It also polymerizes and causes further reaction of the organic matter. When boiling has been completed, this polymerized organic matter in the form of a black pitch rises to the top of the dilute acid solution in the tank. The acid can be drawn off for further use, but the pitch like the other acid sludges is difficult of disposal. The content of the spent acid is reduced by the boiling.

The two processes described above do reduce the volume of the acid sludge and serve to recover much of it as dilute acid which may be utilized in other processes. However, in both cases, a large amount of acid pitch is left, the disposal of which is still a problem.

In accordance with the present invention, there is provided a further improved process, by means of which process the acid sludge referred to above, can be recovered as a neutral, aqueous solution which is handled more easily and can be treated more readily for the recovery of values.

The process of the present invention consists of the following steps:

1. The oil is fractionated carefully to remove as much of the impurities boiling below 80° C. as possible. Their separation is made substantially complete by distilling off 10–20 per cent of the benzene present in the oil as a second fraction which may be utilized in other than pure products.

The distillation is continued and a third fraction of the light oil is collected. This contains the balance of the benzene, the toluene, and the xylene, all of which are to be washed with sulphuric acid. In order to recover the xylene completely, the end point of this fraction may be carried up to between 150° and 160° C. or even a little higher.

2. The crude "benzene, toluene and xylene fraction" is washed with sulphuric acid in the customary manner. After the acid washing is complete, water is added to the agitator, as has been described above in the second acid recovery process. After settling both spent acid and acid sludge are drawn off together into a separator. Here they settle further and the spent acid on the bottom is finally pumped to a third tank. The acid sludge remains in the separator.

3. Ammonia now is added to the acid sludge in the separator, either in the form of a gas or as a more or less concentrated solution of ammonium hydroxide. Mixing is desirable in order to neutralize the sludge uniformly. If the spent acid has been separated carefully from the sludge, the temperature of the system should not rise higher than 70–80° C., but if it approaches the boiling point, admission of ammonia should be stopped and the system cooled.

4. The acid sludge now is in the form of a thin, clear, brown solution, neutral or slightly alkaline with ammonia. Any light oil which the sludge has contained separates as a layer on the surface. The sludge solution can be drained to a storage tank. The water content of this solution will vary because it depends largely on the water content of the neutralizing ammonia. Since the sludge always contains some water, water for solution will be present in case substantially dry ammonia gas is used for neutralization.

The following steps represent an alternative procedure which offers certain advantages over the above, while embodying the principal reactions set forth above:

1. The crude light oil is fractionated as described above.

2. The fractionated oil is washed with acid as in the above method, but only the spent acid is drained from the washer. The acid sludge is left in the oil.

3. Ammonium hydroxide solution is added to the agitator in sufficient volume to neutralize both the acid sludge and the light oil. When neutralization is complete, the solution of acid sludge is settled out and drawn from the washed light oil. This process has the further advantage that the light oil and the acid sludge are neutralized by the same operation.

If desired, other alkalis such as sodium hydroxide or a sodium carbonate may be used instead of ammonia, and, less preferably, lime or magnesia. These last two reactants, however, precipitate insoluble compounds.

The improved process is illustrated by the following illustrative example:

Ten-thousand gallons of light oil were fractionated. The following fractions were collected:

1. 150 gallons of forerunnings, which distilled up to 75° C.

2. 1,000 gallons of crude benzene which contained substantially all forerunnings not separated in the previous fraction.

3. 7,500 gallons of benzene, toluene and xylene distilling up to an end point of 165° C.

4. 1,350 gallons of residue left in the still which may be fractionated further if desired.

The 7,500 gallons of benzene, toluene and xylene were washed with 55 gallons of 66° Bé. sulphuric acid for 30 minutes.

After settling for 15 to 30 minutes, the resulting acid sludge was drawn off to the boiling tank. 175 gallons of 66° Bé. sulphuric acid then were added to the oil, and the two were agitated in contact for one to three hours. From 200 to 400 gallons of water were added, and the agitator was allowed to settle for from 30 minutes to an hour, and both spent acid and acid sludge were drained into the boiling tank containing the previous acid sludge. Both sludges were mixed by stirring for 20 minutes until the dilute acid from the second wash caused a separation of the spent acid and sludge from the first wash. The spent acid solution now was pumped to another tank in which it was boiled with direct steam to separate small amounts of organic matter still dissolved or entrained.

To the acid sludge left in the boiling tank were added 95 gallons of a 20% solution of ammonia, the acid sludge being mixed continuously during admission of the ammonia until neutralization was complete. 142.5 pounds of ammonia were required. The contents of the tank were

allowed to settle and 300 gallons of clear brown solution containing about 25 per cent water were drawn off. 20 gallons of oil were left in the tank and returned to another batch of light oil being washed with acid in the agitator.

The solution produced from the sludge by the above-described procedure is suitable for ready disposal in any convenient manner.

We claim:

1. The process of treating light oils produced in the production of coke from bituminous coal, which comprises fractionating light oil to remove at least the major portion of impurities boiling below 80° C., completing the separation of such impurities by distilling off from approximately 10 per cent to approximately 20 per cent of benzene present in the oil, thereby forming a second fraction, continuing the fractionation of the light oil to produce a third fraction containing the balance of the benzene, together with the toluene and xylene contained in the original light oil, washing this third benzene-toluene-xylene fraction with sulphuric acid, adding water to the resulting washed mixture, withdrawing spent dilute acid from the resulting material, neutralizing the resulting acid sludge with a neutralizing agent selected from the group consisting of alkali hydroxides and alkali carbonates, and separating the resulting neutralized acid sludge as a thin clear solution from the said benzene-toluene-xylene fraction.

2. In a process of treating light oils produced in by-product coking of bituminous coal in order to obtain a water-soluble acid sludge, wherein the light oil is fractionated to remove at least the major portion of impurities boiling below 80° C., the separation of such impurities being completed by distilling off from approximately 10 per cent to approximately 20 per cent of benzene present in the oil, thereby forming a second fraction, the fractionation being continued to produce a third fraction containing the balance of the benzene together with the toluene and xylene contained in the original light oil, the improvement which comprises obtaining an acid sludge capable of forming a thin, clear, aqueous solution, by washing the said third benzene-toluene-xylene fraction with sulphuric acid, adding water to the resulting mixture, allowing spent dilute acid and resulting acid sludge to settle into layers, removing the spent dilute acid and acid sludge from the washed benzene-toluene-xylene fraction, allowing the removed spent dilute acid and acid sludge to separate into layers, separating the resulting layers of spent dilute acid and acid sludge, and neutralizing the acid sludge with a neutralizing agent selected from the group consisting of alkali hydroxides and alkali carbonates, thereby converting the said acid sludge into a thin, clear aqueous solution suitable for disposal.

3. The process of treating light oils produced in the production of coke from bituminous coal which comprises fractionating light oil to remove at least the major portion of impurities boiling below 80° C., completing the separation of such impurities by distilling off from approximately 10 per cent to approximately 20 per cent of benzene present in the oil, thereby forming a second fraction, continuing the fractionation of the light oil to produce a third fraction containing the balance of the benzene, together with toluene and xylene contained in the original light oil, washing this third benzene-toluene-xylene fraction with sulphuric acid, adding water to the resulting washed mixture, withdrawing spent dilute acid from the resulting material, neutralizing the resulting acid sludge with ammonium hydroxide and separating the resulting neutralized acid sludge as a thin clear solution from the said benzene-toluene-xylene fraction.

4. The process of treating light oils produced in the production of coke from bituminous coal as claimed in claim 1, wherein the acid sludge is neutralized with caustic soda, and the resulting neutralized sludge is withdrawn as a thin clear solution from the benzene-toluene-xylene fraction.

5. The process of treating light oils produced in the coking of bituminous coal as claimed in claim 1, wherein the acid sludge is neutralized with sodium carbonate and the resulting neutralized sludge is withdrawn as a thin clear solution from the benzene-toluene-xylene fraction.

6. In a process of treating light oils produced in by-product coking of bituminous coal in order to obtain a water-soluble acid sludge as claimed in claim 2, the step of neutralizing the acid sludge with ammonium hydroxide, thereby converting the said acid sludge into a thin, clear aqueous solution suitable for disposal.

7. In a process of treating light oils produced in by-product coking of bituminous coal in order to obtain a water-soluble acid sludge as claimed in claim 2, the step of neutralizing the said acid sludge with sodium hydroxide, thereby converting the said sludge into a thin, clear aqueous solution suitable for disposal.

8. In a process of treating light oils produced in by-product coking of bituminous coal in order to obtain a water-soluble acid sludge as claimed in claim 2, the step of neutralizing the said acid sludge with sodium carbonate, thereby converting the said sludge into a thin, clear, aqueous solution suitable for disposal.

JOSEPH H. WELLS.
PHILIP J. WILSON, JR.