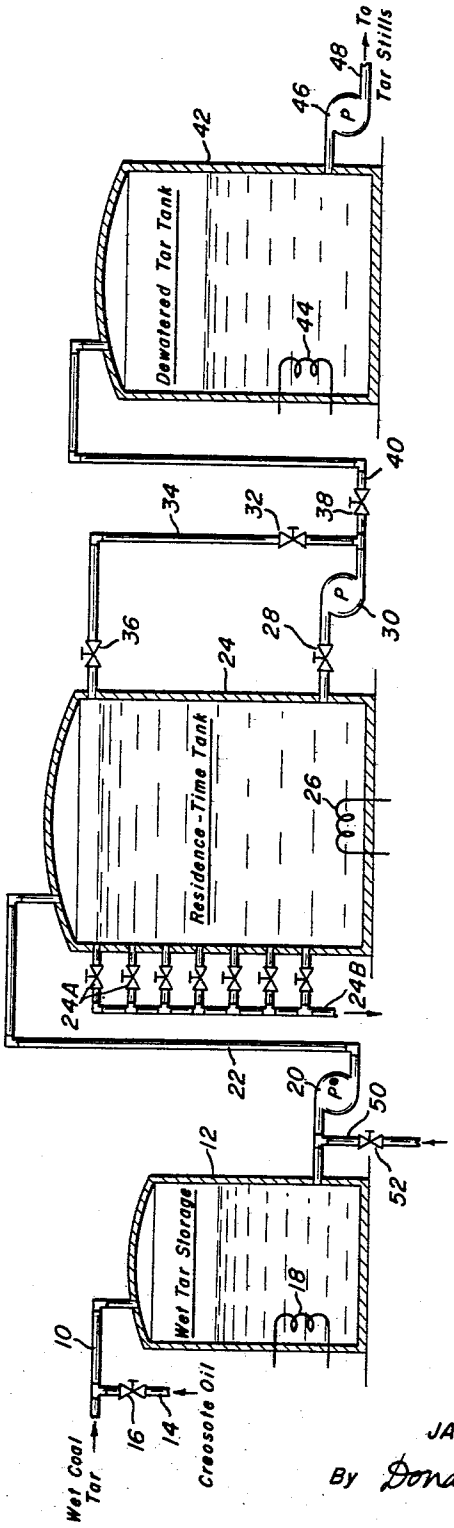
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METHOD OF DEWATERING TAR

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METHOD OF DEWATERING TAR

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This invention relates generally to the recovery of crude coal tar resulting from the destructive distillation of bituminous coal, and more particularly to methods for dewatering the crude coal tar thus produced, improving the subsequent tar distillation and products obtained therefrom.

In conventional coke-plant practice, the foul gas from the coke ovens is cooled by spraying with flushing liquor which, along with the condensible tars and other compounds, flows to a decanter for separation of the liquor from the condensed tar. The flushing liquor is recycled for further gas cooling while the condensed tar is pumped to a wet-tar storage tank. The gas and remaining vapors are further cooled in primary coolers, the condensate comprising tar and liquor being decanted and separated. The tar is pumped to a wet-tar storage tank. Primary-cooler tar is less viscous and has a lower specific-gravity range than flushing-liquor tar. These tars may be combined or separately stored for different end uses. In the method to be described they are combined in a wet-tar storage tank for subsequent dewatering and distillation.

Production of crude coal tar as hereinabove described is effected by condensation of a vapor to a liquid. The condensation results in entrainment of liquor with the tar which does not separate completely in the described decantations, resulting in so-called wet tar. The liquor contains a number of dissolved salts, including ammonium chloride which, in any subsequent tar distillation are deleterious to steel equipment, especially at the higher temperatures attained therein. Prior to any distillation it is preferable to dewater the tar to decrease equipment size and heat requirements. Dewatering also reduces the entrained liquor content and the salts dissolved therein.

In conventional practice various methods of separating the water from high moisture tars have been used. These methods include the use of centrifuges, additives from various outside sources, decanters, and flash-dehydration units. While some of these methods are reasonably successful, they may in turn be expensive and time consuming or the additive may cause difficulties later in the operation, due to disposal or adulteration problems.

I have discovered that numerous advantages over conventional practices are obtained by adding a coal-tar distillate fraction to the heavy, water-containing tar, and agitating the contents of the tank by recirculating the admixture until it is fairly homogeneous. The tank and its contents are then held in a relatively quiescent state, between about 90° and 98° C. for a period of at least about 24 hours, after which time, dewatered tar, containing between about 1 and 3% moisture may be drawn off the bottom. The water or liquor layer, which separates and rises to the top of the tank, may be disposed of by conventional means such as siphoning and removal through cocks on the side of the tank.

It is the generally accepted belief of the chemical industry that the greater the difference between the specific gravities of two liquids, the better will be the resultant phase separation upon gravity settling. While this is generally true, my invention is an exception to accepted principle. This is so because of the relationship I have found between surface tension, viscosity and specific gravity. I have discovered that, with a reduction in the specific-gravity difference between water and tar by the admixture of a coal-tar distillate fraction with wet coal tar, there is substantial improvement both in the speed

and the degree of water separation therefrom. I believe the improved separation occurs because the distillate fraction reduces the surface tension of the tar, allowing the occluded water droplets to ascend to the surface. To increase the mobility of the water droplets an ascending temperature gradient should be maintained from the top of the tar-storage tank to the bottom, between about 90° and 98° C. in order to reduce further the restrictive tar viscosity. Tar recovered from most coke-ovens has a surface tension in a range of about 40 and 42 dynes/cm. Since the procedure for determination of surface tension is delicate and not susceptible to rapid performance for plant control, a correlation has been established between the surface-tension effects and rapidly determinable specific gravity for this purpose, in practicing my invention.

A complete understanding of the invention may be obtained from the following detailed description and explanation which refer to the accompanying drawing illustrating the present preferred practice. The single figure of the drawing is a diagrammatic representation of a system for carrying out the method of my invention.

Referring now in detail to the drawing, wet coal tar is introduced by a pipe **10** from a decanter (not shown) to a wet-tar storage tank **12**, which may be one of a number of such tanks found in a tar plant. The entrained-liquor or water content of the tar may vary widely. It is usually between about 5% and 12% by volume of tar, but may be as high as 20%. The specific gravity thereof may vary between about 1.20 and 1.28 at

$$\frac{15.5^\circ\ C.}{15.5^\circ\ C.}$$

the surface tension being between about 40 and 42 dynes/cm. A coal-tar distillate fraction may be a creosote-oil fraction having a wide range of boiling points (B.P. 200°–350° C.) and preferably is a light creosote oil boiling over a range between about 200° and 310° C., having an average specific gravity of about 1.060 at

$$\frac{15.5^\circ\ C.}{15.5^\circ\ C.}$$

and a surface tension of about 33 dynes/cm. The light creosote-oil fraction is injected through pipe **14** into pipe **10**. Control valve **16** supplies sufficient oil to reduce the specific gravity of the admixture to between about 1.10 and 1.18 at

$$\frac{15.5^\circ\ C.}{15.5^\circ\ C.}$$

The amount of oil admixed with the wet tar may vary between about 5% and 20% (by volume) depending upon the water content of the tar, its initial viscosity, surface tension and specific gravity. Steam coil **18** serves to maintain the effluent-tar temperature between about 75° and 95° C.

The surface tension of the homogeneous admixture should be sufficiently low to release the water droplets occluded in the tar and to permit them to rise. The admixture flowing from the bottom of tank **12** is transferred by pump **20** through pipe **22** into residence-time storage tank **24**. Steam-heating coil **26** serves to maintain the tar-temperature gradient from top to bottom in this tank between about 90° C. and 98° C. This temperature gradient further reduces the viscosity of the wet tar-oil admixture. The mobility of the water droplets is increased and the water-tar separation is thereby facilitated. When storage tank **24** is sufficiently full, the contents are thoroughly mixed by recirculating them through valve **28**, pump **30**, valve **32**, pipe **34**, and valve **36** into tank **24**. When the admixture is fairly homogeneous, as evidenced by a specific gravity variation in the contents of not more than about .02, pump **30** is stopped, valves **28**, **32** and **36**

are closed and the contents of the tank are then held in a relatively quiescent state for a period of at least about 24 hours at the aforesaid temperature gradient, during which time the water separates from the tar and rises to the top of tank **24**. When the water separation is completed, water is drawn off the top of tank **24** through test cocks **24A** and pipe **24B**, whence it returns to the aforementioned decanters or is recycled as flushing liquor for further gas cooling. Tar containing between about 1.8% and 2.2% moisture, or less, flows from the bottom of tank **24** and is moved by pump **30** and pipe **40** into dewatered-tar tank **42**. The dewatered tar flows from the bottom of tank **42** and is delivered by a pump **46** through a pipe **48** to tar stills (not shown) for fractionation and the recovery of pitch.

The above-described, relatively quiescent state continuing for a period of at least about 24 hours at a temperature gradient from top to bottom of the tank between about 90° and 98° C., is termed the residence time. Once established for any tank, the advantages of my invention are obtained by substantially balancing admixture admission and dewatered-tar withdrawal at a rate such as to permit any one gallon of tar to remain in a tank for at least about 24 hours, as its residence time. The longer the residence time over about 24 hours, the better the water-tar separation. However, a practical limit for residence time is about 48 hours, since beyond this time the moisture content of the dewatered tar will not be substantially below about 1%.

A specific example of the practice of the invention giving quantities involved is set forth below.

In a typical coke plant producing about 150,000 gallons of tar per day, the combined flushing liquor and primary cooler tars contain between about 8% and 12% of entrained liquor, have a specific gravity between about 1.22 and 1.24 and a surface tension between about 40 and 42 dynes/cm. The wet tar is pumped through pipe **10** to tank **12**, which may have a capacity of 200,000 to 500,000 gallons. A creosote-oil fraction is pumped through pipe **14** into pipe **10**. This fraction has a boiling range between about 211° and 305° C., an average specific gravity of 1.060 at

$$\frac{15.5^\circ\ C.}{15.5^\circ\ C.}$$

an average surface tension of 33 dynes/cm. The fraction is admixed with the wet tar in a quantity sufficient to produce an admixture having a specific gravity between about 1.14 and 1.16 at

$$\frac{15.5^\circ\ C.}{15.5^\circ\ C.}$$

The quantity of the fraction admixed is between about 8% and 10% by volume of the wet tar dependent upon the source of the original tar. Coil **18** heats the admixture in tank **12** to between about 85° and 95° C. The admixture is pumped to a 1,000,000 gallon dwell-time tank **24** and recirculated by pump **30** until the admixture is fairly homogeneous, that is, until the specific gravity thereof does not vary much more than .02 between successive pump samples. Should the specific gravity of the admixture be greater than about 1.16, additional light creosote oil may be added to the admixture in tank **24** through pipe **50**, valve **52**, pump **20** and pipe **22**. After thorough mixing, the contents of tank **24** are kept relatively quiescent for about 24 hours. The temperature gradient from top to bottom of tank **24** is maintained between about 90° and 95° C. Thereafter, dewatered tar having a moisture content between about 1.8 and 2.2% is withdrawn from tank **24** and pumped to tank **42** or directly to a still (not shown) at a rate of about 100 gallons per minute. The separated liquor is removed through cocks **24A** and the input and output of the tank are balanced.

While the above example illustrates a preferred method of operation, other conditions of operation may be used without departing from the spirit of the invention. The admixture in the wet-tar storage tank will vary in temperature between about 75° and 95° C. according to the season and liquor content. The temperature will normally be maintained higher in colder weather and as the liquor content increases, to aid in the separation of the liquor. It is preferable for good mixing to add to the wet tar a coal-tar distillate fraction through pipe **14**, although the total fraction or any additional fraction required to attain a preferred admixture specific gravity may be made through pipe **50**.

It should not be assumed from the above, that it is mandatory to have a quiescent period of at least about 24 hours before more wet-tar-oil admixture is pumped to the tank and dewatered tar is withdrawn therefrom for distillation. After a fairly homogeneous admixture is established in tank **24** and the quiescent period begins, it has been found that an 8–12% moisture tar will have had its moisture content reduced to about 4–5%. Balanced input and output may commence immediately, the sole requirement being that the quantities involved should permit a dwell time of at least about 24 hours before admixture in the top of the tank is withdrawn as dewatered tar from the bottom thereof. During this period, the optimum reduction in the moisture content will be progressively attained.

Any fraction having a specific gravity between about 1.04 and 1.12 at

$$\frac{15.5^\circ\ C.}{15.5^\circ\ C.}$$

may be used. While I prefer an admixture having a specific gravity between about 1.14 and 1.16, admixtures having a specific gravity between about 1.10 and 1.18 may be employed. Below about 1.10 specific gravity, improved surface tension effects will be overshadowed by the danger of creating troublesome emulsions. Above about 1.18 specific gravity, water separation will become progressively more difficult since the surface tension of the admixture approaches that of undiluted tar. Ordinarily, the fraction is admixed to between about 8% and 10% by volume of the wet tar, the maximum being about 20%. The fraction, whatever its boiling range and gravity, is totally miscible in all proportions with the tar.

The maximum amount of a fraction admixed is usually determined by the size of distillation and handling equipment in an existing tar plant. Ordinarily, beyond a threefold increase in any boiling-range fraction over that naturally occurring in undiluted tar will require the uneconomic reduction in overall admixture throughput in the tar still. The so-called wide-boiling range creosote oil fraction (B.P. 200° C.–350° C.) comprising light- and heavy-creosote oils may be admixed. The light creosote oil is preferred for its more pronounced, surface-tension effects. Narrow-boiling fractions, for example, a tar-acid fraction or a methyl-naphthalene fraction may be used to advantage, if the economics permit. It must be understood, however, that the cheapest wide-boiling fraction is effective. Any further fractionation thereof adds to the cost of obtaining a narrow-boiling fraction or product.

It has been found that the viscosity of an admixture with flushing-liquor and primary-cooler tars will be reduced sufficiently to permit efficient separation of liquor with bottom heating to between about 95° and 98° C. Within the practical limits of a temperature gradient of about 90° and 100° C. between top and bottom, a higher-viscosity flushing-liquor tar, when treated alone, should be heated to the high side of this range, and a lower-viscosity primary-cooler tar to the low side of the range. Basically, one adds as much heat as is required, to the bottom of the tank, without allowing any boiling to occur. Depending on such factors as the type and quantity of the contents, this will produce a temperature at the top of the tank between about 85° and 95° C.

The invention is characterized by several distinct advantages. In the first place, the separation of liquor and tar is a relatively simple, inexpensive and efficient process,

as compared to former practices. Suitable wide-boiling or narrow-boiling fractions are readily available in any coal-tar plant. A fraction may be recovered through distillation in unchanged form and may be reused indefinitely. Wet tar with a liquor content of 5% to 12%, and higher, can be reduced consistently to between about 1% and 2.5% liquor content.

Secondly, the addition of a coal-tar fraction improves tank cleaning and heating. The fraction is a solvent for the binders holding coke and coal dust into a sludge-form requiring frequent tank cleaning. Additionally, binder removal permits the coke and coal dust to move with the tar and increases the quinoline- and benzene-insoluble content of pitch distilled from the tar. In the production of special electrode pitches this is desirable and reduces the need for addition of pulverized material.

Thirdly, my process can be easily varied to handle separately, flushing-liquor tar and primary-cooler tar, the former having both a higher viscosity and specific-gravity range. Utilizing the principles of this invention, tars with viscosities outside these limits may be processed.

Finally, an operator may be faced with a sudden and even prolonged period of excessively high liquor content in the incoming wet tar. In such an emergency one or more of the principles taught by my invention may be utilized. In the wet-tar tank and/or the residence-time tank there may be admixed a greater volume of a coal-tar fraction. There may be a change to a fraction that will produce a lower surface tension in the admixture. The temperature gradient and residence time may be increased. Where there is a greater than preferred variation in specific gravity, the residence-time tank may be recirculated. Were there assurance that such an emergency would never occur, it would be possible to eliminate the wet-tar tank, the dewatered-tar tank and operate solely with a residence-time tank.

Although I have disclosed herein the preferred practice of my invention, I intend to cover as well any change or modification therein which may be made without departing from the spirit and scope of the invention.

I claim:

1. A method of dewatering wet coal tar comprising admixing therewith a coal-tar creosote-oil fraction, conducting the admixture to the top of a storage tank, maintaining an ascending temperature gradient in said admixture from the top of said tank to the bottom while allowing the admixture to separate, conducting separated liquor from the top of said tank and dewatered tar from the bottom thereof.

2. A method as defined in claim 1, characterized by admixing sufficient of said creosote-oil fraction to produce

an admixture having a specific gravity between about 1.10 and 1.18 at

$$\frac{15.5^\circ\ C.}{15.5^\circ\ C.}$$

3. A method as defined in claim 1, characterized by said creosote-oil fraction having a boiling range between about 200° and 350° C.

4. A method as defined in claim 1 characterized by recirculating the admixture in said storage tank, prior to allowing the admixture to separate, until the contents thereof have a specific gravity variation of no more than about .02.

5. A method as defined in claim 1, characterized by maintaining said temperature gradient between about 90° and 98° C.

6. A method as defined in claim 1, characterized by substantially balancing dewatered tar withdrawal and admixture admission to said tank and at a rate such as to permit a residence time for the admixture of at least about 24 hours.

7. A method of dewatering wet coal tar containing between about 5% and 12% entrained liquor by volume, comprising admixing therewith sufficient coal-tar creosote-oil fraction having a boiling range between about 200° and 310° C. to produce an admixture having a specific gravity of between about 1.14 and 1.16 at

$$\frac{15.5^\circ\ C.}{15.5^\circ\ C.}$$

conducting the admixture to the top of a storage tank, recirculating the admixture in the tank to mix it until substantially all of it is in said range of specific gravity, maintaining an ascending temperature gradient in said admixture from the top of said tank to the bottom of between about 90° and 98° C., substantially balancing liquor withdrawal from the top of said tank plus dewatered tar withdrawal from the bottom thereof with admixture admission to said tank and at a rate such as to permit a dwell time for the admixture of at least about 24 hours.

8. A method as defined in claim 1, characterized by distilling dewatered tar and recovering pitch, thereby removing binders for sludge-forming, quinoline- and benzene-insolubles in the tar and substantially reducing sludge formation while dewatering tar and recovering pitch with an increased content of said quinoline- and benzene-insolubles.

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