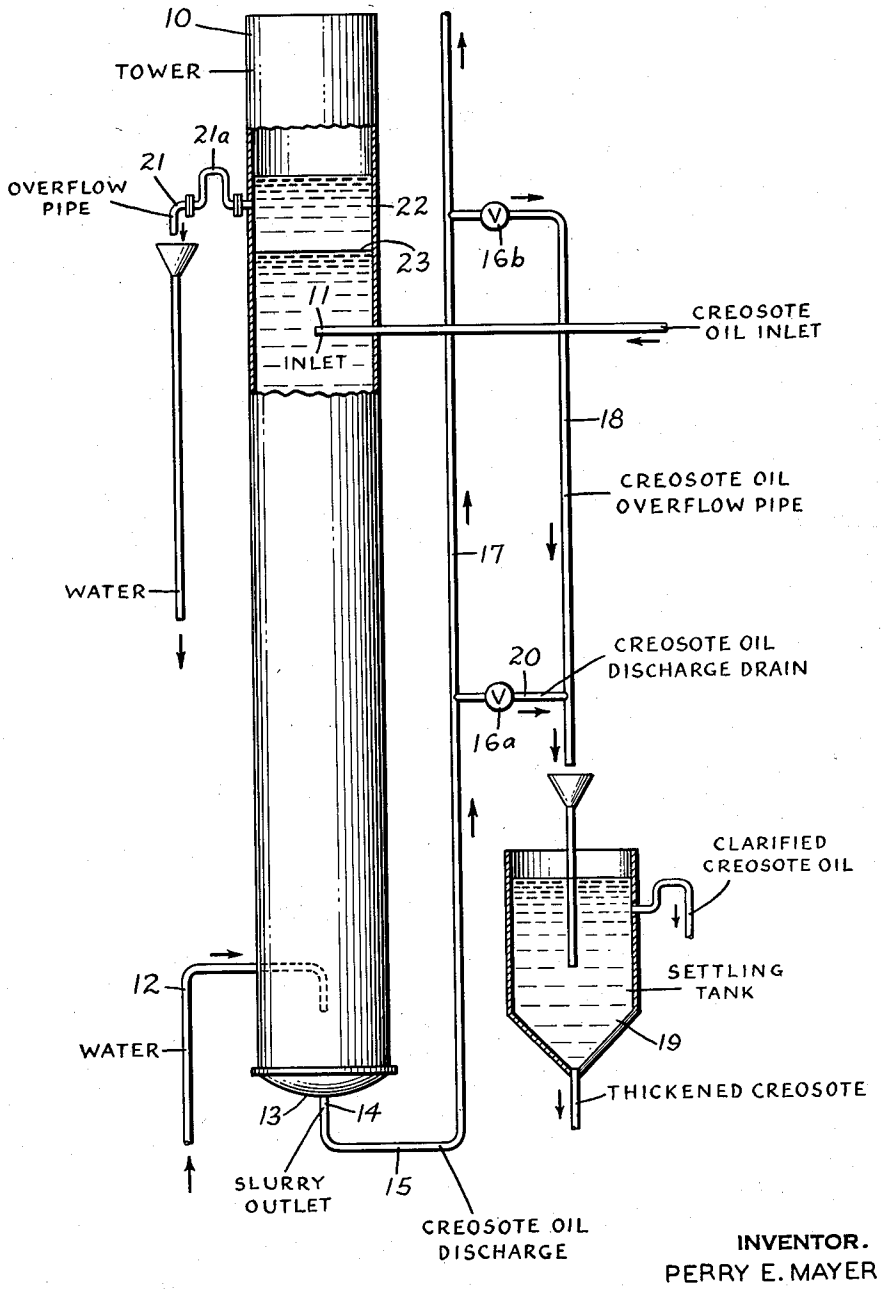
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CONTINUOUS PROCESS FOR CLARIFYING CREOSOTE OILS

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CONTINUOUS PROCESS FOR CLARIFYING CREOSOTE OILS

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This invention relates to a process for clarifying creosote oils, and more particularly to a process for preparing creosote oils which will remain liquid during storage and shipment under normal industrial conditions.

The so-called "Creosote oils" include, in general, distillates of coal gas tar and coke oven tar, and have been known and used for many years for a variety of purposes. The term "creosote oils" therefore, refers to a variety of oils of extremely complex chemical composition and physical properties, and these attributes vary markedly with the source of the oil, the distillation process by which it was recovered and other factors concerning its history. For example, the coal gas tars and coke oven tars are usually distilled to produce at least two fractions, a "light" or low boiling fraction, a "heavy" or high boiling fraction, and sometimes a medium fraction as well, in addition to the "pitch" or tarry residue which remains in the still. The resulting oils are then often "topped" or otherwise treated to recover a portion of certain selected types of compounds therefrom such as "tar acids" i. e. phenols, cresols etc., "tar bases" i. e., heterocyclic nitrogen bases, a naphthalene fraction, etc.

The oils marketed as "creosote oils" may be constituted of all or part of the original distillate, or, as is often the case, they may be blends of distillates which have been treated in other recovery operations. These extremely complex mixtures are sold for a variety of uses, one of the largest and most important of which is for wood preservation by treatment of the wood with the creosote oil by suitable methods, which may include brushing, spraying, immersion, or the like, with or without the aid of vacuum or pressure treatments.

If the original distillation of the tar has been carried out to form a hard pitch, e. g., if the tar has been heated at temperatures up to about 355° C. or above to remove a large percentage of the high boiling oils from the residue, the proportion of such high boiling compounds in the resulting "heavy" and "medium" oils will be high, and such compounds may also be present to some extent in the lighter oils as well.

Such crystallizable compounds occur as mixtures of a variety of compounds including anthracene, carbazole, phenanthrene and the like. They are usually colloquially characterized as "anthracene salts", and are valuable by-products, useful in the manufacture of dyes and the like. Many creosote oils, especially oils containing high percentages of crystallizable compounds, although fluid when freshly prepared, often precipitate a portion of the crystalline "anthracene salts", on storage or shipment under prevailing industrial conditions, especially in the winter months when temperatures are low. This crystal separation is extremely troublesome and costly because it complicates pumping of the oils and emptying of tank cars, and also occasions losses in total oil delivered due to the fact that a portion of the initially measured oil remains as a crystalline residue on the inside walls of the tank car unless the tank car is heated to remove the accumulation of solids.

These difficulties have led to many attempts in the past to treat or "clarify" the creosote oils to preserve their liquidity.

Creosote oils of the character described have been treated or "clarified" in the past to produce oils of higher liquidities by a number of methods including storage for long periods during which crystallizable compounds, the "anthracene salts," precipitated from the oil and settled to the bottom of the storage vessel. Another prior clarification method involved slowly cooling the oil in large agitated vessels equipped with internal cooling coils, followed by separation of the crystallized solids from the oil, usually by centrifuging. Another method utilized an outside heat exchanger with pump circulation to effect slow cooling of the oil. In still another method, the oil was passed through a tank or tower equipped with exterior cooling means and rotating side scrapers to remove the crystals from the walls of the tank, and the resulting crystal slurry was passed to a centrifuge to separate crystals from mother liquor. All of these processes had the disadvantage of high cost, either for storage or for refrigeration, and, due to the tendency of the crystals to coat the cooling surfaces and form an insulating layer which restricted passage of heat to the cooling medium, made the processes employing refrigeration largely impracticable.

Efforts to avoid the disadvantages of crystal build-up on the cooling surfaces by increasing the rate of cooling (shock cooling) as by increasing the temperature differences between oil and cooling surface, or by increasing agitation or circulation rate, resulted in the formation of extremely fine crystals which were difficult or impossible to separate from the oil by practical means. Moreover, while it has been known that certain liquid hydrocarbons, including molten naphthalene, could be cooled to the point of crystallization by contacting them with immiscible liquids such as water, such cooling methods have not been considered applicable to the cooling of creosotes because of the strong tendency of the creosotes to occlude water in emulsion or other form and thus make difficult the subsequent separation of water to produce the required "water-free" product.

It is an object of the present invention to provide a process for clarifying creosote oils which avoids the disadvantages of the prior art processes.

A further object is to provide a continuous process for the crystallization and removal of crystallizable components from creosote oils to such an extent that the resulting oil remains fluid under prevailing industrial conditions of storage and shipment.

A still further object is to provide a process for continuously producing clarified creosote oils of a wide range of desired liquidity characteristics.

A still further object of the invention is to provide a process for lowering the limpid point of a creosote oil.

A still further object is to provide a process by which creosote oils of low fluidity may be processed continuously for the production of high fluidity oil and valuable anthracene salts.

A still further object is to provide a process for rapidly cooling creosote oils to produce anthracene salt crystals of relatively large, free draining, easily separable character.

These and other objects are accomplished according to my invention wherein countercurrently flowing streams of creosote oil and water are brought into direct heat exchanging relationship with each other in a contacting zone under such conditions that partial crystallization of a portion of the oil is effected, and large free draining crystals are formed.

Contacting of the mutually immiscible oil and water may be effected, according to my invention, in any suitable manner which insures the desired degree of heat exchange within temperature and time ranges within which

large, free draining crystals are formed of components whose removal will leave a resulting creosote oil of the desired liquidity characteristics.

Liquidity characteristics of creosote oils are customarily measured in terms of the so-called "limpid point (out)," which is the temperature at which the first crystals appear when the oil is cooled from a higher temperature. Another characteristic sometimes used in evaluating cresote oils is the "limpid point (in)" which is the temperature at which the last crystals of a cresote oil-crystal slurry dissolve when the slurry is heated. Whenever the term "limpid point" is used in the trade without qualification, it usually refers to "limpid point (out)," and will be so used in the present specification. This temperature of "limpid point (out)," is usually used as synonymous with the temperature of complete liquidity.

Thus when a creosote oil is cooled from a temperature which is above its "limpid point (out)" temperature, to a temperature below such point, crystals will form, whose separation results in an oil of lower limpid point. Continued cooling and separation of crystals will continue to lower the limpid point of the resulting oil still further until the desired limpid point lowering has been effected.

In carrying out the limpid point lowering of creosote oils according to my invention, water which is at a temperature below the limpid point out of the creosote oil to be treated, and which is preferably substantially free of dissolved gases under pressure, is introduced continuously into a body of creosote oil in such a manner as to avoid attaining the critical injection velocity which would cause emulsification, and to cause gentle, smoothly flowing streams or globules of water to form which pass slowly through the oil, cooling the oil below its initial limpid point and causing crystallization of at least a portion of the components. In a preferred embodiment of the invention, hot creosote oil is continuously fed into a vertical column of creosote oil, and, due to its greater specific gravity, passes downwardly through the ascending streams of water droplets during which time a portion of its heat is absorbed by the water. Crystallization is usually initiated somewhat below the point of introduction of the creosote oils, and crystal formation and growth continue during the passage of the oil through the column, the cooling rate decreasing somewhat as the creosote oil moves down the column, allowing time for crystal growth in the cooler, more viscous creosote. After contact of the oil with the water is complete, the resulting oil-crystal slurry is continuously withdrawn to a slurry receiver. The crystals may be separated from the slurry in any desired manner, for example by centrifuging or filtering the slurry immediately, or if desired by first allowing time for settling of the crystals, followed by decanting the supernatant oil, and mechanically separating the crystals from the thickened slurry, aided if desired, by washings with hot water to separate entrained oil from the crystals.

A particular advantage of the process is that creosote oils at temperatures considerably above their limpid point temperatures, for example at 80° to 90° C. or higher, as they come from the stills or blending vessels may be fed directly to the clarifying tower without a separate cooling step and the hot creosote oil may be cooled down to the point of initial crystallization (its "limpid point out" temperature) rapidly by contact with the ascending cooling water and by the supernatant pool of water which collects above the heavier creosote oil. In such cases the process combines a two stage cooling and crystallization effect in a single continuous process; the first stage being the rapid cooling of the hot creosote oil to its limpid point temperature, the second stage being the controlled slow cooling of the oil during the crystallization stage.

The resulting creosote oil will possess a limpid point which is lower than that of the original oil, the degree of lowering being dependent on conditions used, as explained hereinafter, and will be substantially free of water. The recovered crystals of "anthracene salts" may be further purified and resolved into their component compounds including anthracene, carbazole, etc.

The water which has been used to effect the direct cooling and crystallization of the creosote oil is substantially uncontaminated and may be reused, after cooling, for further creosote oil treatments.

Any of the class of oils known as creosote oils may be treated according to my invention to effect a lowering of their limpid points and to improve their liquidity including so-called light, medium and heavy creosote oils. My invention is particularly adapted for use in treating oils of this character which have specific gravities greater than 1, i. e., that are heavier than water, and is especially advantageous in treating the heavier oils resulting from carrying tar distillations to harder pitches, and which oils thus have relatively high percentages of components boiling above 355° C. These latter oils cannot be adequately clarified by current clarification process to produce commercially acceptable creosotes which will remain fluid under industrial conditions of storage and shipment.

While the creosote oils contemplated for treatment according to my invention are extremely complex and have widely varying characteristics, they may be defined generally as distillates of coal gas tar or coke oven tar or fractions or mixtures thereof having boiling ranges predominantly within the range between about 200° C. and about 400° C., and having specific gravities of between 1.03 and 1.18. Many of the light creosote oils boil or distill completely within the range between about 200° C. and about 355° C., while others, such as the so-called medium and heavy oils notably the creosote oils from hard pitch distillations, may contain up to 50% of components distilling at 355° C. and above.

The water used in direct cooling of the creosote oil should preferably be substantially free of dissolved gases, such as air, under pressure. If such gases are present when the water is introduced in the creosote oil column, the release of pressure at the time of such introduction will tend to liberate gas bubbles within the body of the creosote oil where they may become trapped, so lowering the effective density of the oil that it may cease to flow by gravity through the column. If water as received at the process site contains such dissolved gases under pressure, it may readily be released by suitable means, as by vacuum degassing or by simply releasing the water into an open tank to release excess gas under pressure.

The cooling water used should preferably be introduced into, and caused to flow upwardly through the column of creosote oil in gentle smooth-flowing streams of globules (as distinct from jets or sprays), to avoid emulsion formation. This smooth flow may be accomplished, for example, by providing water distributor openings large enough to avoid the critical injection velocities responsible for emulsification, and, to avoid clogging of the water inlets with "anthracene salts" it may be advantageous to orient the inlets in the direction of the creosote flow, for example to locate them on the under side of a pipe or sparger type distributor.

The choice of operating conditions will of course depend on the final limpid point characteristics desired in the clarified oil. Any conditions which reduce the temperature of the oil from a temperature above its "limpid point (out)" to a temperature below the "limpid point (out)" will effect some crystallization and consequent limpid point lowering of the oil obtained on separation of the crystals, and such conditions, therefore, are within the scope of my invention. In clarifying creosote oils for commercial use, it is usually desirable to effect a lowering of the limpid point of the oil to a value which will insure maintenance of its liquidity under the particular industrial conditions to which the oil will be sub-

jected. For such purposes, in general, it will usually be sufficient to reduce the "limpid point out" to about 10° C., although creosote oils for special purposes may be required to remain crystal-free at 5° C. or even lower temperatures. For other purposes, less drastic liquidity requirements are imposed. Conditions which can be controlled to effect the desired limpid point lowering and which are interrelated are (*a*) the relative initial temperatures of creosote oil and water, (*b*) the rates of water and creosote flow and (*c*) the initial limpid point of the creosote oil.

The quantity of water needed to promote optimum conditions for crystallization is surprisingly small. It depends on the above interrelated factors chiefly (*a*) the rate of creosote flow (*b*) the temperatures of the water and of the creosote supplied to the crystallizer, (*c*) the temperature at which crystals start to form when the creosote is cooled (i. e. the limpid point out) and (*d*) the degree of limpid point lowering to be effected, a quantity of water equal to between about ¼ and about ¾ the weight of creosote oil usually being sufficient.

The respective initial temperatures of the counter-currently flowing creosote oil and water employed, will depend on the characteristics of the creosote oil being treated and on the characteristics desired in the clarified oil product, as well as on the rate of flow and contact time of the two liquids. The initial temperature of the creosote oil will be at least equal to its "limpid point out" temperature, usually somewhat above.

The initial temperature of the water will be below the limpid point of the particular creosote oil, and enough below, to effect the desired limpid point lowering under the conditions of operation. Temperatures down to about 0° C. may be used.

The highest temperature present in the contacting zone will be at about the point of creosote oil introduction, and the upper temperature limit in the effective crystallizing zone will desirably be maintained only slightly above the temperature at which crystallization starts in the particular oil being clarified, i. e. the so-called "limpid point (out)" of the oil. Temperatures appreciably lower than limpid point temperatures at this point, tend to promote the formation of fine crystals which are difficult to separate from the oil. Temperatures appreciably above limpid point temperatures at this point are unnecessary and wasteful of heat exchanging space and media in cooling the oil to its limipid point temperature.

Temperatures at any given point in the contacting zone will depend on the initial temperatures of the contacting liquids, the length of the contacting zone, and the relative flow rates of the liquids.

The cooling rate of the creosote oil is important in producing large, free-draining crystals which can readily be removed from the clarified creosote oils. One of the primary difficulties which has prevented adoption of the rapid cooling processes in the past is the tendency of such processes, involving large temperature differences between oil and coolant, to produce extremely fine crystals which were difficult or virtually impossible to separate from the viscous creosote oils by reasonably practicable methods.

In the process of my invention, even in cases where creosote oils at high temperatures are introduced into the heat exchanger, crystallization is initiated slowly in the upper portion of the contacting zone where the cooling water is at a temperature below the "limpid point (out)" of the creosote oil but not sufficiently below to cause formation of large quantities of fine crystals, preferably not more than about 5° C. below the limpid point of the particular creosote oil, usually about 1° to 3° C. below. Such crystals as are formed, act as nuclei for crystal growth as the creosote is further cooled during its passage through the crystallizing zone.

The cooling rate in the crystallizing zone, therefore, will be slow enough to prevent crystallization in the form of fine, virtually inseparable crystals, but rapid enough so that clarification of the oils may be effected in periods appreciably shorter than have heretofore been possible, a temperature drop of between about 6° C. and about 15° C. per hour usually being satisfactory.

In general there appears to be a minimum retention time, which may vary with the particular creosote oil, necessary to result in the formation of satisfactorily large crystals for ready separation from the oil in commercial equipment. In general a minimum of at least about 3 hours is required, a period between about 3 hours and about 6 hours usually being sufficient if final temperatures of the cooled creosote oil are not taken below about 20° C. Longer times are required if lower temperatures are to be attained.

The temperature range through which the creosote oils are cooled will vary somewhat depending on the final limpid point desired in the clarified creosote oil. Cooling of creosote oils from above their limpid point out temperatures to a point of at least about 20° C. below their limpid point out temperatures results in substantial improvement in the liquidity of the oil and in many cases is sufficient to effect the desired clarification upon removal of the crystals formed.

The lowest temperature to which the creosote is to be cooled will depend on the degree of limpid point lowering desired. In general the final limpid point will be found to be appreciably lower than the temperature to which the creosote is cooled, according to the process of my invention, by as much as between about 10° and about 20° C. Thus, to produce a creosote oil having a limpid point between about 5° C., and about 10° C., it is usually sufficient to cool the creosote oil to about 20° C. If a lower final limpid point is desired, lower final cooling temperatures may be employed.

Initial limpid points of the various creosote oils adapted to be clarified according to my invention range from about 80° C. to as low as about 40° C. It is usually sufficient for commercial purposes to reduce the limpid point of the oils to between about 5° C. and about 10° C. to produce oils which remain liquid under conditions of industrial storage and shipment. Such oils as are produced from hard pitch distillations usually have limpid points (out) between about 80° C. and about 60° C. and thus require controlled cooling through a temperature range of a maximum of about 60° C. usually of about 40° C. or less, for example from about 70° C. to about 20° C., and in these ranges cooling rates averaging between about 6.5° C. and about 10° C. per hour have been found satisfactory.

Thus, starting with the desired minimum retention time necessary to form readily separable crystals, and using water at an entering temperature suitable to produce the desired final limpid point in the clarified creosote oil as explained above, corresponding factors may readily be calculated for use in various sized equipment according to the following equation.

$$\text{Retention Time (Hours)} = \frac{\text{Height of crystallizing zone (inches)} \times \text{Volume of creosote per unit of length (gals/in.)}}{\text{Rate of creosote flow (gals/hr.)}}$$

Any suitable apparatus may be used for carrying out the process according to my invention. The apparatus may be of conventional type. A satisfactory arrangement is that used in carrying out the clarifications described in the examples which follow and schematically illustrated in the accompanying drawing.

In the drawing, **10** represents a well insulated cooling tower provided with a creosote oil inlet **11** near the top of the tower and a water inlet **12** near the bottom of the tower. The bottom **13**, of the tower, which may be rounded or conical, is equipped with an outlet **14**, connected to a discharge pipe **15**. The discharge pipe **15**

may be connected either to a discharge leg 17 which in turn connects through valve 16*b* by means of overflow pipe 18 with settling tank 19; or, it may be connected directly, through valve 16*a* and pipe 20 with settling tank 19. At the upper end of the tower, a water overflow pipe 21 adjustable by means of a swivel 21*a* is positioned in water layer 22 above the creosote oil level 23 for removing the water after it has passed through and above the creosote oil column.

EXAMPLES

In the examples which follow apparatus of the character described above was used in which the insulated tower was 6 inches in diameter by 19 feet high. Runs of 30 to 60 hours duration were made on each of six different creosote oils (oils 1 to 6 inclusive).

In carrying out the runs the crystallizing tower was filled about three-quarters full of creosote which had been previously clarified. The levels were then permitted to equalize in the tower and leg. The creosote pump was started, feeding hot creosote into the crystallizing tower through a short nipple in the side wall extending into the tower at a point about 16 feet above the water inlet and two feet below the water overflow. The creosote feed was controlled to give a downward flow in the tower of three to four feet per hour. Cooling water at 8–20° C. was started and the rate adjusted as required to maintain desired temperature gradient. Water was introduced through a single one-half inch nipple on the side wall, extending to the center and turned downward, at a level approximately one foot from the bottom of the tower. The distance of 16 feet between water and creosote inlet points fixed the effective cooling height of the unit. Within a few seconds after starting the water into the tower it separates and collects in a pool on the surface of the creosote. When the rise in level in the tower is sufficient to compensate for the greater density of the cooler creosote in the discharge leg, the latter overflows and discharges the cooled slurry to the receiver. The water overflow level of the pool on top of the creosote was adjusted to maintain this equilibrium with a water layer depth of 6 to 18 inches. A one-half inch nipple for discharge of water was located above the creosote oil-water interface to avoid removing the creosote film on the surface.

Occasional adjustments of the water discharge nipple were necessary to compensate for gravity changes in the creosote and maintain the desired water layer depth and corresponding creosote oil levels in the tower. A small interface float (not shown), responding to creosote level changes only, guided these adjustments. By lowering the water level (decreasing the height of liquid in the tower) the creosote level would rise, decreasing the depth of the water layer. Best results were obtained when the fresh hot creosote was introduced into the creosote zone in the crystallizer and not into the water layer. About three hours after starting, the creosote collected up to that time representing the initial filling charge was withdrawn from the receiver and stored to start the next run. A few fine crystals were usually found in this creosote near the change period. A period of two to three hours' operation, after the starting creosote charge had been displaced, was usually sufficient to bring the crystallizer to normal conditions, requiring very little attention beyond the maintenance of creosote and water flows to the unit and disposal of the cooled slurry from the receiver. The practice followed in shutting down was to stop the feed and water pumps, allow about 30 minutes to complete the separation of water and creosote in the unit, and then drain the creosote back to the feed tank. By stopping the creosote pump only, the body of creosote in the crystallizer could be cooled and discharged to the regular receivers by gradual displacement by the cooling water.

The creosote slurries were thickened in a 22-inch diameter drum with a cone bottom. The flow of slurry from the continuous crystallizer entered through a feed pipe extending downward in the drum to the top of the cone. Thickened slurry containing 10 to 20 percent solids was withdrawn from the bottom of the cone at hourly intervals. Clarified creosote was recovered continuously (except for brief periods after each under-flow) through side arm arrangements around the top of the drum and just below the creosote surface, preventing any water that collected on the thickener from discharging with the water-free clarified creosote.

The recovery of creosote was completed on a 26-inch diameter perforate basket suspended centrifuge. The feed slurry of 10 to 18 percent solids content was stored in a 100-gallon agitated vessel installed above the centrifuge. Wire filter cloths of 30 x 30 square mesh per inch were used as a filter medium in the centrifuge and gave good filtration rates and were free from plugging by greases and waxes present in many of the creosotes. Sturdier screens such as the 12 x 64 mesh per inch Dutch weave also give good results.

The basket was brought to loading speed of 750 R. P. M. (corresponding to a centrifugal force of 200 times gravity) and the feed valve opened full. Filtration was rapid for two to three minutes, before sedimentation and compression of the crystals decreased the filtration rate. Frequently, the basket speed was increased near the end of the loading cycle to maintain the filtration rate and complete the filling of the basket. Loading times ranged between five and eleven minutes for the various creosotes. The installation of a multi-hole nozzle plate on the feed pipe to distribute the slurry over the filter screen prevented sedimentation in the bowl and aided in filling an evenly loaded basket.

After loading was completed, a whizzing cycle of six to twelve minutes at 1,500 R. P. M. (800 times gravity) was sufficient to dry the cake. The crystals retained 10 to 20 percent of creosote as determined by pressing at 6,000 pounds pressure between absorbing paper.

Improved creosote yields were obtained by washing the 60 to 70 pound load of filter cake in the centrifuge basket with 150 to 175 pounds of water at 90° to 95° C. Washing required about two minutes to four minutes. The initial drying time (after loading) was reduced when washing was carried out so that the overall cycle was not increased appreciably.

The washed salt retained only two to four percent of residual creosote. This creosote, about one gallon per load, separated practically completely from the wash water in one to two hours.

The physical characteristics of the creosote oils used in runs 1 to 6 respectively are given in Table 1 together with the physical characteristics of the clarified oil resulting therefrom after removal of the "anthracene salt" crystals. Of these oils Nos. 1 and 2 are "medium" oils, No. 3 is a "heavy" oil, No. 4 is a special "light" oil, No. 5 is a carbolic oil residue (a "light" oil) and No. 6 is a "light" oil.

Table No. 1.—Physical characteristics of creosote oils used in Examples 1–6

OIL NO. 1

Distillation, ° C.	Charged, Percent	Clarified, Percent
0–210	0.1	0.1
210–235	3.0	2.6
235–270	15.0	10.7
270–315	17.6	16.9
315–355	25.8	22.4
Over 355	34.6	47.4
Sp. Gr. 80° C./15.5° C.	1.136	
Limpid Point, ° C.:		
In	61.5	19
Out	50.0	9
Water, Percent	0.15	0.2

OIL NO. 2

Distillation, ° C.	Charged, Percent	Clarified, Percent
0–210	0.0	0.0
210–235	3.3	5.3
235–270	7.0	16.8
270–315	18.2	18.8
315–355	33.2	26.2
Over 355	34.5	32.9
Sp. Gr. 15.5° C./15.5° C	1.134	
Limpid Point, ° C.:		
In	68.0	24
Out	56.0	10
Water, Percent	0.15	0.10

OIL NO. 3

Distillation, ° C.	Charged, Percent	Clarified, Percent
0–210	0.0	0.0
210–235	1.5	0.6
235–270	1.7	4.7
270–315	12.2	12.8
315–355	26.4	19.9
355 C. and over	52.2	58.9
Sp. Gr., 15.5° C./15.5° C	1.160	
Limpid Point, ° C.:		
In	70.0	22.0
Out	59.0	7.0
Water, Percent	0.15	0.3

OIL NO. 4

Distillation, ° C.	Charged, Percent	Clarified, Percent
0–210	0.0	0.0
210–235	1.8	3.5
235–270	14.5	18.7
270–315	23.2	23.7
315–355	22.3	23.4
355 C. and over	31.9	26.8
Sp. Gr., 15.5° C./15.5° C	1.114	
Limpid Point, ° C.:		
In	57	20.0
Out	49	5.0
Water, Percent	0.05	0.15

OIL NO. 5

Distillation, ° C.	Charged, Percent	Clarified, Percent
0–210	0.0	0.0
210–235	4.1	0.0
235–270	17.8	34.8
270–315	42.0	32.5
315–355	24.5	20.3
355 C. and over	8.8	8.1
Sp. Gr., 15.5° C./15.5° C	1.096	
Limpid Point, ° C.:		
In	81.10	24
Out	68.0	9

OIL NO. 6

Distillation, ° C.	Charged, Percent	Clarified, Percent
0–210	0.0	0.0
210–235	0.3	0.0
235–270	11.5	18.4
270–315	31.9	30.2
315–355	33.1	28.5
355 C. and over	17.3	19.4
Sp. Gr., 15.5° C./15.5° C	1.081	1.084
Limpid Point, ° C.:		
In	72	39
Out	64	24
Water, percent	.08	.01

Operating data showing the respective flow rates and initial temperatures of creosote and water and temperatures at various locations within the crystallizing zone are given in Table 2 below, zero location being a point just above that at which crystallization is initiated.

Table No. 2—Operating data oils 1–6

Oil No.	Temperatures in ° C. at various Tower Locations (Inches from oil inlet) Within Crystallizing Zone							Flow Rate Gallons Per Hour		Tower Retention Time, Hours
	Water Inlet	167	119	71	24	0	Oil Inlet	Creosote	Water	
1	15	19	24	31	43	52	70	4.7	2.3	4.3
2	13	24	31	40	52	59	80	6.7	3.3	3.0
3	15	24	29	40	50	55	79	5.2	2.6	4.0
4	8	15	20	29	42	52	78	4.4	3.0	4.6
5	12	21	27	35	43	48	77	4.6	2.4	4.4
6	20	31	37	44	52	57	77	4.8	2.0	4.2

Yields of creosote oils and anthracene salts from the several runs are given in Table 3 below.

Table No. 3.—Yields of creosote oils and anthracene salts obtained in runs 1–6

Oil No.	Time, Hours	Rate, Gal./Hr.	Percent	
			Salt	Creosote
1	69	4.7	4.7	95.3
2	60	7.3	9.7	90.3
3	59	4.3	10.5	89.5
4	36	4.4	6.1	93.9
5	40	4.6	9.4	90.6
6	56	5.4	7.4	92.6

The process of my invention provides distinct advantages over prior art processes of creosote oil clarification and limpid point lowering, in that it provides a rapid process for obtaining high yields of limpid creosote oil, leaving little or no residual oil in the anthracene salts (1% or less). It is a commercially practicable, relatively inexpensive process; it is adapted to continuous operation, with reuse of all process waters, and therefore presents no waste disposal problems, and it is applicable to a wide variety of creosote oils to produce greater or lesser degrees of limpid point lowering at will.

While the above describes the preferred embodiments of my invention, it will be understood that departures may be made therefrom within the scope of the specification and claims.

I claim:

1. A process for treating creosote oils to improve their liquidity which comprises causing countercurrently flowing creosote oil having a "limpid point out" of at least about 40° C. and water to contact each other in direct heat exchanging relationship in a contacting zone whose temperature ranges from an upper limit which is above the "limpid point out" temperature of the oil to a lower limit which is at least about 20° C. below the "limpid

point out" temperature of said oil, whereby free draining crystals are formed, and separating the crystals from the oil.

2. A process for clarifying creosote oils to improve their liquidity which comprises causing countercurrently flowing creosote oil having a "limpid point out" of at least about 40° C. and water to contact each other in direct heat exchanging relationship in a contacting zone whose temperature ranges from an upper limit which is above the "limpid point out" temperature of the oil to be clarified to a lower limit which is at least about 20° C. below the "limpid point out" temperature of said oil whereby crystals are formed, said contacting taking place over a period of time sufficient to insure the growth of large free draining crystals, and separating the clarified oil from the resulting crystals.

3. A process for clarifying creosote oils to improve their liquidity which comprises continuously passing water upwardly through, and in direct heat exchanging contact with, a column of downwardly flowing creosote oil having an initial "limpid point out" above about 40° C. the initial temperature of the oil being above its "limpid point out," the initial temperature of the water being at least about 20° C. below the "limpid point out" temperature of the oil, whereby crystals of a portion of the oil components are formed, said contact of oil and water taking place over a period of time sufficient to produce large free draining crystals, and to reduce the temperature of the creosote oil from above its "limpid point out" temperature to a least about 20° C. below its "limpid point out" temperature and separating the clarified oil from the resulting crystals.

4. A process for clarifying creosote oils to improve their liquidity which comprises continuously passing water upwardly through, and in direct heat exchanging contact with, a column of downwardly flowing creosote oil having an initial "limpid point out" between about 80° C. and about 40° C., the initial temperature of the oil being above its "limpid point out," the initial temperature of the water being between about 0° C. and about 20° C., whereby free draining crystals of a portion of the oil components are formed.

5. A process for clarifying creosote oils to improve their liquidity which comprises continuously passing water upwardly through, and in direct heat exchanging contact with, a column of downwardly flowing creosote oil having an initial "limpid point out" between about 80° C. and about 40° C., the intial temperature of the oil being above its "limpid point out," the initial temperature of the water being between about 0° C. and about 20 C., whereby crystals of a portion of the oil components are formed, said contact of oil and water taking place over a period of time of at least about 3 hours to produce large free draining crystals, and at a rate of flow to produce cooling of the creosote oil at a rate of between about 6.5° C. and about 10° C. per hour from its "limpid point out" temperature to a final temperature at least about 20° C. below its "limpid point out" temperature, and separating the clarified oil from the resulting crystals.

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