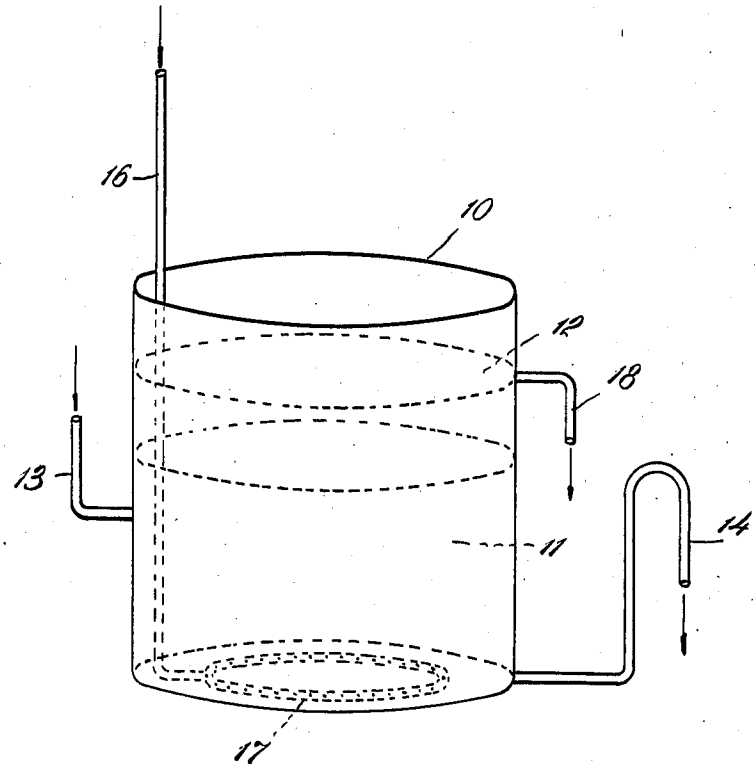
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TREATMENT OF CREOSOTE

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TREATMENT OF CREOSOTE

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This invention relates to the treatment of coal tar creosote and particularly to the treatment of creosote derived from coal by the "direct" process in which the creosote is subjected to the temperatures prevailing in distillation for only a short period of time, of the order of four to five minutes.

Coal tar creosote, particularly that derived by the "direct" process, tends to deteriorate upon ageing. In order to be saleable as first grade material, it must fulfill certain rigid specifications, and frequently coal tar creosote which fulfilled these specifications at the time it was produced, fails to conform after a period of several weeks of storage or ageing. Thus, coal tar creosote which originally had a "coke residue" content below the usual tolerable limit of 2.00% may deteriorate upon storage until its coke residue content exceeds this limit, in which case the creosote is no longer saleable, at least as first grade material. That this tendency toward deterioration of coal tar creosote in storage is a recognized one is evidenced by the requirements of some users that the creosote shall meet specifications at the time of use, as well as at the time of shipment from the producing plant.

As a result of our investigations, we have discovered that coal tar creosote may be prevented from deteriorating and in fact actually improved in quality by maintaining it in contact with a liquid aqueous body (such as a pool of water which may or may not contain dissolved material) at relatively low temperatures (such as those normally encountered in stored creosote) for a considerable period of time and out of contact with oxidizing influences. The more thorough and intimate is the contact between the creosote and the water, the greater is the improvement of the character of the creosote. Thus, deterioration of coal tar creosote can be prevented completely and the grade of the creosote slowly improved by storing it in a tank at atmospheric temperatures under a layer of water. However, more rapid improvement in grade may be obtained by passing water through the body of the creosote into the overlying water layer, thereby increasing the surface of contact between the water and the creosote.

The action of the aqueous body appears to be twofold in that it acts as a seal and protects the creosote from oxidizing influences, such as air, and also may leach from the creosote certain harmful substances which, if allowed to remain, tend to bring about excessive deterioration of the creosote. These and other features of our invention will be understood more readily in the light of the following detailed description of our presently preferred practices, taken in conjunction with the accompanying single figure which illustrates one form of apparatus adapted for storing or treating the creosote in accordance with our invention.

Coal tar creosote must fulfill rigid requirements for specific gravity, water content, percentages distilled at various temperatures, residue after distillation, specific gravity of various fractions distilled, coke residue, tar acid content, flash point, etc. An effort has been made to standardize these specifications, but some variation is found for specifications in various grades of creosote and also in the specifications set up by various consumers. However, practically all specifications, regardless of grade of creosote or of the particular consumer, require that the coke residue of the creosote shall not exceed 2.00%. Especially when the creosote as produced closely approaches the upper limit of 2% coke residue, this specification is likely to be exceeded during a period of storage or shipment, so that the creosote becomes unsaleable as first quality oil. Other characteristics of the creosote, as exemplified by the foregoing items of specification, may also suffer unfavorable changes if the creosote is allowed to stand for a considerable time prior to use, and our invention contemplates preventing deterioration of the creosote with respect to these characteristics and also contemplates improving creosote with respect to these characteristics.

Creosote ordinarily is stored in large cylindrical tanks. Storage of quantities exceeding 100,000 gallons in a single tank is common practice. An easy method for practicing the invention with creosote stored in such tanks is to introduce a layer of several inches of water into the tank. The water is substantially immiscible with the creosote and has a lower specific gravity so that it floats as a layer on the creosote in the tank and thus seals it from the air. At the same time, solution of undesirable ingredients of the creosote takes place at the interface between the water and the creosote and these ingredients when once dissolved in the water no longer exert their harmful influence upon the creosote. A more rapid removal of the undesirable ingredients and greater improvement in the character of the creosote may be obtained by increasing the surface of contact between the water and the creosote in the tank. This may be done conveniently by introducing the water in a relatively finely divided state below the surface of the creosote and per-

mitting it to rise upwardly through the creosote to the overlying water seal. In its progress through the body of creosote the water tends to leach out the undesirable ingredients and brings about a rapid and permanent improvement in the character of the creosote and particularly in its coke residue content.

The improvement in the character of creosote obtained in the practice of our invention is contrasted with the deterioration which is experienced with similar material when it is permitted to stand under ordinary conditions exposed to the air. As an example of heretofore customary practice in the storage of creosote, a body of creosote amounting to 150,000 gallons was permitted to stand in a tank at a temperature of about 25° C. but in contact with air at its upper surface for a period of four weeks. As the following analysis shows, the material in the beginning of the storage period was of high grade and had a coke residue content well below the limit of 2%. However, during storage the material deteriorated substantially with the result that it no longer fulfilled specifications and was unsaleable as first-grade material.

Table No. I

Sample	Original	After storage
Specific gravity	1.052	1.059
Per cent driven off—distillation to 210° C	4.6	2.7
Per cent driven off—distillation to 235° C	20.2	16.4
Per cent driven off—distillation to 315° C	59.0	55.0
Per cent driven off—distillation to 355° C	80.5	78.0
Per cent distillation residue	19.4	21.6
Per cent coke residue	1.91	2.14

Another batch of creosote amounting to 100,000 gallons was allowed to age for a period of three weeks in a tank under conditions precisely similar to those described above, except that the creosote was covered by a layer or seal of water about 2 inches thick and amounting to 900 gallons. During this three week period, as the following Table No. II shows, there was an improvement in the character of the creosote. Thus, the original coke residue content of 2.05% was reduced during storage to 1.82% after three weeks treatment so that the material was brought into a first grade condition.

Table No. II

Sample	Original	After 2 weeks storage	After 3 weeks storage
Specific gravity	1.050	1.050	1.051
Per cent driven off—distillation to 210° C	4.0	3.3	3.8
Per cent driven off—distillation to 235° C	22.6	21.9	21.9
Per cent driven off—distillation to to 315° C	64.0	63.2	62.2
Per cent driven off—distillation to to 355° C	85.1	84.0	83.1
Per cent distillation residue	14.5	15.5	16.7
Per cent coke residue	2.05	1.97	1.82

Referring now to the drawing, it will be observed that the apparatus comprises a large cylindrical tank **10** which is disposed vertically. The tank preferably should be of large diameter in relation to its height so as to provide a large surface for contact between the water and the creosote. A body of creosote **11** is maintained within the tank, and it is overlain by a layer of water **12** which seals the creosote from the air. If desired, a relatively continuous flow of creosote may be maintained through the pool by introducing creosote through an inlet line **13** which enters the tank adjacent the top of the creosote pool, creosote being withdrawn from the bottom of the tank through a gooseneck **14**. The gooseneck is so constructed that its top is at approximately the same level as the upper surface of the creosote pool, so that a constant and predetermined level of creosote is maintained within the tank. Water is introduced into the tank through a vertical pipe **16** which is connected with a perforated hollow ring **17** in the bottom of the tank. The ring may conveniently be made of pipe. The perforations in the ring are small so that the water enters in minute streams and gives a maximum contact surface with the surrounding creosote. The water is substantially immiscible with the creosote and rises upwardly through the pool thereof into the overlying water layer from which it may be overflown through an outlet pipe **18** connected to the side of the tank.

It will be observed that in the apparatus a countercurrent flow of creosote and water may be maintained, if desired. On the other hand, if it is unnecessary to purify the creosote extensively and rapidly, and it is merely necessary to prevent its deterioration, or bring about a slow improvement in grade, no flow of water or creosote through the tank need be maintained, in which case the tank is merely a storage reservoir in which the creosote is protected and slowly beneficiated by the overlying water layer.

The degree of improvement which results from the mere storage of creosote under a protective water layer is well illustrated by the comparative results given in the foregoing Table No. II. This improvement is, however, brought about relatively slowly, and more rapid improvement is obtained in the character of coal tar creosote by increasing the surface of contact between the water and the creosote beyond that provided by the interface of the creosote pool and the overlying water layer. This may be brought about in various types of apparatus such as scrubbing towers and the like, but ordinarily it is not necessary to employ such complex equipment and the apparatus illustrated in the figure will give excellent results. In one instance, illustrated by the figures in the following Table No. III, 11,000 gallons of water were passed upwardly through an 1100 gallon batch of creosote in a period of three hours. Originally, the coke residue content of the creosote was 2.09%. This was reduced to 1.81% during the three hours contact period.

Table No. III

Sample	Original	After treatment
Specific gravity	1.060	1.059
Per cent distilled at 210° C	1.2	2.6
Per cent distilled at 235° C	15.8	17.0
Per cent distilled at 315° C	56.0	56.8
Per cent distilled at 355° C	80.0	82.3
Per cent distillation residue	19.5	17.3
Per cent coke residue	2.09	1.81
Flash point, °F	177.0	189.0
Float test	46.0	39.0

In the treatment exemplified by Table No. III, the apparatus corresponding to that shown in the figure was employed. The water was introduced as finely divided streams within the body of the creosote and rose therethrough to the overlying water seal layer.

It will be observed that in addition to improvement with respect to coke residue the "distillation residue" of the creosote was also decreased

by the treatment. Moreover, the flash point of the creosote was raised and the float test results were improved. All of these are desirable changes in grade and indicate an improvement in the general quality of the creosote which is obtained when the water is percolated through the creosote.

While we do not subscribe to any particular theory as to how the water brings about the improvement in the creosote, we are inclined to believe, as indicated hereinbefore, that it acts in a twofold manner. In the first place, the water layer acts as a seal and protects the creosote from oxidizing influences. In the second place, the water in contact with the creosote apparently leaches out undesirable ingredients which have a tendency to bring about an increase in the coke residue content. Analysis of water which has remained in contact with creosote in accordance with our invention shows a substantial content of both ammonia and phenol. It is probable that these substances or chemical combinations thereof, such as the comparatively simple ammonium phenate, or one or more complex phenol amines exert a deleterious influence if allowed to remain in the creosote. In any event, the removal of these ingredients from the creosote not only prevents its deterioration but actually brings about an improvement in its grade.

In the process of our invention a greater degree of beneficiation results when the creosote treated is that derived by flash distillation in a direct recovery process. In such a process, coal tar remains at distillation temperature for a very short time, probably not in excess of four to five minutes. In contrast, tar distilled in an old type batch still remains in the still and in a heated condition for a fairly long time, from six to forty-eight hours being required for the preparation of a batch of creosote by this means. It is probable that during the longer heating in the batch still method, many of the compounds which otherwise would form "coke residue" in the creosote during the storage thereof are formed in the still and remain with the tar. On the other hand, in a flash distillation process the formation of these compounds is not completed in the still, but tends to take place slowly in the creosote during storage. The formation of these compounds, with a consequent increase in coke residue content of the creosote, is promoted by heat or by oxidizing influences. Consequently, in the practice of our invention, it is necessary to maintain the creosote at relatively low temperatures, preferably at temperatures as low as 20° C. and in no case at temperatures high enough that a substantial proportion of the creosote is vaporized. Moreover, mere treatment with water without sealing the creosote from oxidizing influences ordinarily is not beneficial.

As indicated hereinbefore, ordinary water with or without dissolved mineral salts, etc., is an adequate treating agent. However, various chemicals including anti-oxidants may be included in the water, if desired. In this connection, it may be observed that the phenol leached from the creosote by the water apparently exerts an anti-oxidant action when present in the latter.

We claim:

1. In the treatment of coal tar creosote containing ammonia and phenol, the improvement which comprises passing water upwardly through a body of the creosote while the latter is in a liquid condition and at a relatively low temperature and out of contact with oxidizing influences until a substantial proportion of the ammonia and phenol has been leached out of the creosote and dissolved in the water and the coke residue content of the creosote is substantially reduced.

2. In the treatment of coal tar creosote containing ammonia and phenol, the improvement which comprises passing water upwardly through a body of the creosote in liquid condition and at a relatively low temperature and out of contact with oxidizing influences and so leaching out of the creosote and dissolving into the water a substantial proportion of the ammonia and phenol, the water being passed upwardly through the creosote until the coke residue content of the creosote is substantially reduced, the water being passed into a layer of water overlying the body of creosote and in contact therewith.

3. In the treatment of coal tar creosote containing ammonia and phenol, the improvement which comprises passing the creosote in liquid condition and at a relatively low temperature in countercurrent contact with water while maintaining the creosote out of contact with oxidizing influences, the creosote being passed in countercurrent contact with the water until the coke residue of the creosote is substantially reduced and a substantial proportion of the ammonia and phenol has been leached out of the creosote.

4. In the treatment of coal tar creosote containing ammonia and phenol, the improvement which comprises passing water in a liquid condition and at a relatively low temperature through a body of creosote maintained at a relatively low temperature until a substantial proportion of the ammonia and phenol has been leached out of the creosote and the coke residue content is substantially reduced, the creosote being protected from the action of oxidizing influences during the treatment with the water.

5. In the treatment of coal tar creosote containing ammonia and phenol, the improvement which comprises passing a fine stream of water upwardly through a body of the creosote maintained at a relatively low temperature and out of contact with oxidizing influences until a substantial proportion of the phenol and ammonia has been leached out of the creosote into the water and the coke residue content of the creosote is substantially reduced, the water being passed through the creosote into an overlying layer of water.

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