

June 18, 1935.

J. V. E. DICKSON

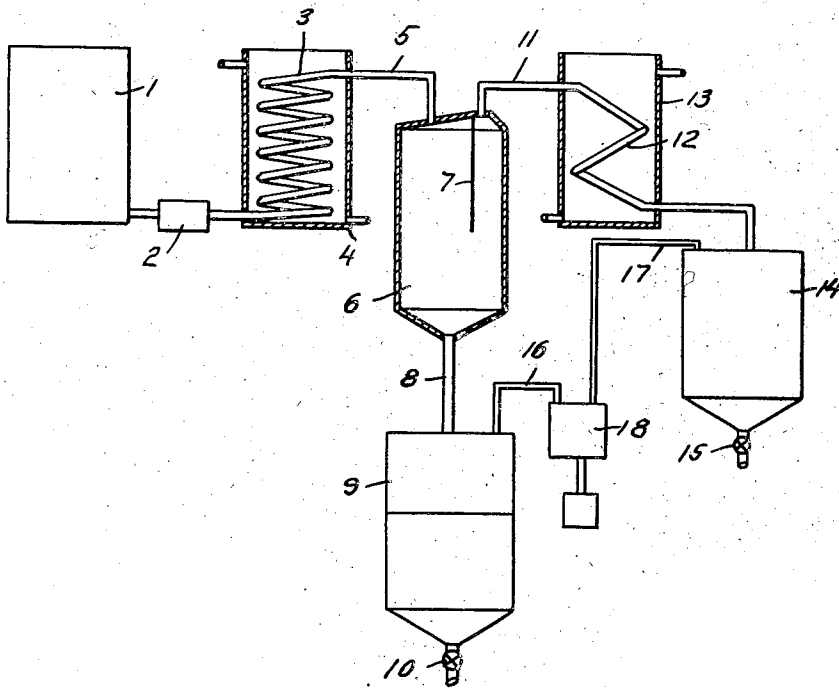
2,005,077

COAL TAR OIL AND PITCH

Filed June 12, 1931

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Fig. 1.



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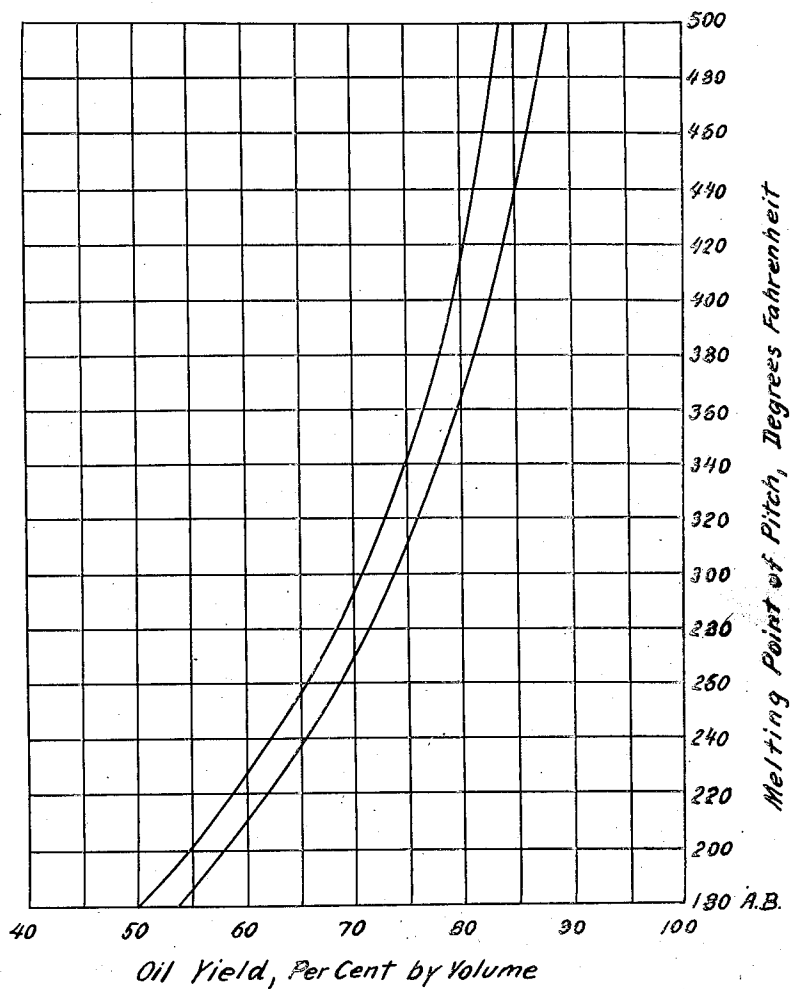
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Fig. 2.



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2,005,077

COAL TAR OIL AND PITCH

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Application June 12, 1931, Serial No. 543,777

10 Claims. (Cl. 196—149)

This invention relates to new tar oils and pitches, and more particularly, to the coal tar oils and pitches produced by the practice of the process disclosed and claimed in my copending application Serial No. 618,772, filed February 13, 1923, issued as Patent No. 1,321,144. This application is directed to and claims the new tar oils and pitches disclosed in the aforementioned copending application, Serial No. 618,772, and bears a continuation in part relationship to this copending case.

As pointed out in application Serial No. 618,772, it has been found that if coal tars are distilled in such a way that they are exposed to unusually high temperatures during distillation, or are heated at the usual distillation temperatures for unusually long periods of time, the total oil recoverable as distillate from them is less than usual, and also the residual pitch is of higher melting point than usual, after a given percentage of oil has been removed as distillate. This may be attributed to decomposition of oils and heavy constituents, including constituents which are normally of a greasy or resin-like character, present in coal tar with consequent formation of increased carbon content, higher melting point pitches, and decreased oil yields.

The oils removed as distillate are almost always of higher commercial value than the residual pitches, and it is therefore desirable to carry out the distillation in such a way that either the maximum total yield of oil will be attained, or the highest possible percentage of oil will be removed before any given commercial grade of pitch has been formed.

The use of "tube stills," such for example as is disclosed on pages 485, 486, et seq. of the fifth edition, Part I of "Coal Tar and Ammonia" by Geo. Lunge, Ph. D., published by The D. Van Nostrand Company, 1916, wherein the tar is heated as it passes continuously through a series of tubes, and is finally discharged into a chamber where the oil vapors and pitch residue separate, has been found to increase the total removable distillate and also to give a pitch residue of lower melting point on the removal of a given percentage of distillate, as compared with the use of the ordinary discontinuous method of distillation, where a charge of tar is heated to boiling and the various oils pass over successively, in vapor form to a condenser. Since approximately the same temperatures are attained in both processes, it is supposed that the difference in oil yields is due principally to the difference in the time during which the tar is heated, which is commonly about ten hours in the discontinuous method of less than one hour in the tube still.

Lowering the distillation temperatures, in the discontinuous method, by (a) carrying on the distillation under greatly reduced pressure (50

mm. of mercury, absolute pressure, or less), or (b) the rapid passage through the tar of a gas having no chemical action on it, has been found to produce results practically the same as those attained in the tube still.

Accordingly, it might well have been supposed that in any one of the three above methods (tube still, reduced pressure, or passage of gas) approximately the optimum conditions had been reached, with regard to the total oil yield attainable or the oil yield attainable in the manufacture of any given pitch from a high temperature tar such as coke oven, or horizontal or vertical retort tars.

However, I have discovered that, in a tube still, (a) by a sufficiently great further reduction of the time during which the tar is heated, greatly increased yields of distillate oil can be obtained, in the production of a given commercial grade of pitch; and (b) if, in addition to thus shortening the time, advantage be taken of the known boiling-point-lowering effect of reduced pressure (by artificially reducing the pressure in the separating chamber), a total yield of distillate can be obtained which is far in excess of that produced by any previously used means known to me.

For instance, a coke-oven tar of a type which usually gives a maximum oil yield of about 45% by weight in the commercial simple discontinuous method and about 65% by weight in the other improved methods mentioned above, has in the new method yielded as much as 80% by weight; and in making most commercial grades of pitch, as judged by their melting points, the difference in oil yield between the new method and the other improved methods amounts to the equivalent of 35-15% of the tar used.

These results are accomplished by heating the tar as it passes through one or more tubular paths or zones, and discharging it at substantially its maximum temperature into a chamber or zone of relatively large volume and correspondingly low pressure compared with said heating zone; where the oil vapors separate from the residual pitch, the vapors passing on into a condensing system and the pitch flowing out continuously at the bottom of the separating chamber. It is important, however, that the time occupied by the tar in traversing the heated tubes should be very short. Since it would be very difficult to measure or to calculate the actual mean time taken by a particle of tar to traverse such an apparatus (because of the expansion due to rise of temperature, and the vaporization of oil taking place continuously during a considerable part of the travel), an indirect way of defining this length of time relatively must be used, and this will consist in defining the ratio of the cubic contents of the tubing traversed to the volume of the tar passing through it in unit time.

If the unit of volume be the cubic foot, and the unit of time be the minute, this ratio will indicate the mean time which would be occupied by a particle of tar in passing through such a piece of apparatus. This ratio for commercial tube stills is commonly about 60, but in the present invention it is not more than 10, and may be much less, or in other words, the tar is passed through the heating tube or zone in amounts not less than one-tenth of the cubical capacity of said heating tube or zone per minute.

In order to reduce the ratio to such low values, particular attention must be paid to the manner of supplying heat. A low value of this ratio means that a comparatively large quantity of tar is being heated per minute in an apparatus of comparatively small volume capacity; and this necessitates an intense and concentrated application of heat. This invention is not limited to any particular method or means of supplying heat to the tubing through which the tar flows, but in the accompanying drawings is illustrated a form of apparatus, in which the heat may be supplied to the tubing by means of a bath of molten metal or alloy through which the tubing passes. The rapidity with which heat passes from a liquid to a metal in contact with it (as compared with the relatively slow passage of heat from a gas to a metal) permits a relatively large quantity of heat to pass per minute into the tube walls (and thence to the tar) without recourse to the very high temperatures in proximity to the tubes which would be necessary in order to transfer heat at such a rate if the tubes were heated by direct contact with furnace gases.

As pointed out above, the process of this invention minimizes decomposition of the tar undergoing distillation, and for a given melting point pitch, results in a greater oil yield than was heretofore obtainable in the distillation of like tar to produce a pitch of like melting point. Hence, both the oil and pitch of this invention differ from and represent novel and useful products as compared with oils and pitches resulting from distillation of coal tar in accordance with prior existing processes. The oils differ from heretofore known oils in that they contain constituents, such as the greasy, resinous, and other heavy constituents, previously decomposed during the distillation of the tar. These heavy constituents blend with the lighter components forming a homogeneous liquid. The oils are suitable for use as creosote oil and for other uses to which ordinary coal tar distillates may be put.

The coal tar pitch, on the other hand, contains a greater proportion of coal tar constituents, as such, and less products of decomposition than a pitch produced by prior known methods since, as pointed out above, decomposition of the tar is minimized in accordance with this invention.

The losses due to decomposition of tar constituents, and therefore the advantages of my invention, are more marked in distilling to pitches of higher melting point; I have obtained especially good results in distilling tar by my method to pitches of melting points of approximately 237° F. and above.

The coal tar oils of my invention comprehend oils produced by the distillation of tar by passage through a tube still at a rate not less than one-tenth the cubical capacity of the still per minute or by other process minimizing decomposition in which the percentage oil yield by volume of the tar distilled bears such relationship to the melting point of the pitch, expressed in

degrees Fahrenheit that x is equal to not less than

$$87 - \frac{128}{2^{\frac{y}{100}}}$$

in which x equals the oil yield in percentage by volume and y equals the melting point of the pitch, expressed in degrees Fahrenheit. Preferably the coal tar oils of this invention are oils obtained by distilling tar while minimizing decomposition of the tar to result in a percentage oil yield by volume falling in the neighborhood of or within the limits defined by the equations—

$$x = 87 - \frac{128}{2^{\frac{y}{100}}}$$

and

$$x = 90 - \frac{128}{2^{\frac{y}{100}}}$$

in which x equals the oil yield in percentage by volume and y equals the melting point of the pitch in degrees Fahrenheit. Likewise the invention includes pitches resulting from the distillation of tar while minimizing decomposition thereof so that the oil yield obtained bears the relationship to the melting point of the pitch indicated above.

The equation—

$$x = 87 - \frac{128}{2^{\frac{y}{100}}}$$

represents the average minimum percentage oil yield by volume for corresponding melting point pitches expressed in degrees Fahrenheit obtainable by the practice of this invention. The other equation—

$$x = 90 - \frac{128}{2^{\frac{y}{100}}}$$

represents the average maximum percentage oil yields by volume for corresponding melting point pitches expressed in degrees Fahrenheit obtainable by the practice of this invention. As more fully pointed out hereinafter, the equations provide definitions of applicant's novel pitches and oils.

In the accompanying drawings, Fig. 1 depicts diagrammatically, an arrangement of apparatus for practicing the process in question and Fig. 2 is a graph illustrating mathematically the relation of the melting point of the pitch to oil yield of the new pitches and new oils obtained by the distillation of tar in accordance with this invention. The abscissæ represent percentage oil yields by volume based on the tar distilled and the ordinates represent pitch melting points in degrees Fahrenheit (air bath method).

In Fig. 1, reference character 1 designates a tank for a supply of tar which may be pumped by means of the pump 2 through the tube 3 which is immersed in a bath of molten metal or hot liquid metal, such as mercury, lead, or other metal of low melting point, in the tank 4. The metal in this tank may be kept in the molten state by heating the same in any convenient way as, for example, by flames impinging upon the bottom of the tank 4, or by passing hot products of combustion through pipes passing through tank 4. A pipe 5 leads from the coil 3 to a sep-

separator 6 for pitch and vapor which is provided with a baffle plate 7. The pitch settles in the bottom of the separator 6 and passes through the pipe 8 into the pitch receiver 9 from which it may be withdrawn through the valve 10. The vaporized constituents pass from the separator 6 through the pipe 11 into the coil 12 in the condenser 13 where they are condensed and passed to the oil receiver 14 from whence the oil may be removed through the valve 15. The receiver 9 for the pitch and the receiver 14 for the oils are connected by pipes 16 and 17 to a vacuum producing means 18.

As the tar is fed into the coil 3, it passes upwardly and is heated by the heat transmitted from the molten metal while it is in transit through the coil 3. The amount of heat supplied will be sufficient to cause the desired amount of distillation to take place. The rate at which the tar is passed through coil 3 will be maintained as indicated above so as to produce an increased yield of oil or distillation in proportion to the amount of pitch or residue that is left.

The following are two examples out of many others that might be given to illustrate how the process has actually been carried out.

(1) A yield of distillate of 58% by weight, corresponding to 62% by volume, with a pitch residue having a melting point of 237° F. has been produced at atmospheric pressure in the separating chamber, with a discharging temperature of about 810° F., and a rate of tar flow of about 70% of the cubic capacity of the heating tube, per minute. The pitch residue consisted of 42% by weight of the coal tar distilled.

(2) A yield of distillate of 75% by weight, corresponding to 78.7% by volume, of pitch residue having a melting point of 352° F. and produced with a discharging temperature of 740° F., and a rate of tar flow of about 38% of the cubical capacity of the heating tube per minute, the separating chamber being maintained at an absolute pressure of 55 mm. of mercury. The resultant oil has a specific gravity of 1.125. The residual pitch constituted 25% by weight of the tar distilled, containing 45.1% volatile combustible material and 39.5% free carbon.

In both of the above examples, a coke oven tar was used, which by ordinary distillation gives about 35% by weight of distillate in producing a pitch having a melting point of 237° F., and in an ordinary tube still or in the recirculated gas method gives about 46% in making a pitch of the same melting point.

It is not practical to make a pitch having a melting point of 352° F. by either the ordinary still or the ordinary tube still method because of danger of coking, but the highest yields customarily obtained from such a tar by these methods are about 40% by the former and 58% by the latter in making a pitch of melting point about 300° F.

The curves of Fig. 2 represent the relationship between the percentage yield of oil and the melting point of the pitch obtained by the practice of this invention. The oil yields and the pitches, of course, vary somewhat, depending upon the particular tar distilled and the differences in conditions under which the distillation operations are conducted. The left hand curve, viewing Fig. 2, corresponds to the lower range of yields by volume of oil obtained by the distillation of tar in accordance with this process to produce pitches of melting points in degrees Fahrenheit indicated on the curve. The right hand curve, viewing Fig.

2, corresponds to the higher range of yields by volume of oil obtained by the distillation of tar in accordance with this invention to produce pitches of melting points in degrees Fahrenheit indicated on this curve.

The left hand curve was obtained by plotting average minimum percentage oil yields by volume obtained as a result of the distillation of tar in accordance with this invention as abscissæ against the corresponding pitch melting points as ordinates. The right hand curve, viewing the figure, was obtained by plotting the average maximum percentage oil yields by volume obtained as a result of the distillation of tar in accordance with this invention as abscissæ against the corresponding average pitch melting points as ordinates. Any point in the area between the two curves represents the percentage oil yields by volume and the corresponding melting point of the pitch in degrees Fahrenheit which may result by the practice of this invention.

$$x = 87 - \frac{128}{2^{100/y}}$$

is the mathematical equation corresponding to the left hand curve and

$$x = 90 - \frac{128}{2^{100/y}}$$

is the mathematical equation corresponding to the right hand curve. Points in the neighborhood of or within the area defined by the equations represent the percentage oil yields which may be obtainable, by the distillation of tar in accordance with this invention, for the production of certain melting point pitches expressed in degrees Fahrenheit. Conversely, for a definite melting point pitch, expressed in degrees Fahrenheit, the equations indicate the percentage oil yields obtainable by distilling coal tar in accordance with this invention. It will be noted, therefore, that the equations provide a definition of applicant's novel distillate oil and pitches, indicating the increased percentage oil yields obtainable in the production of a given melting point pitch.

The products of the present invention include a wide range of pitches and oils and pitches of various boiling points as well as oils of various characteristics. Both the oils and pitches are substantially free from the tar decomposition products, particularly those ordinarily produced by long continued distillation or by exposing tar to unusually high temperatures during distillation and contain constituents of coal tar decomposed by the usual processes of distillation. It will be understood that heavy tars or lighter tars or tarry oils can be distilled to produce the products of this invention. In the case of high temperature tar, such, for example, as coke oven tar, the tar distilled may be the total tar produced in the coke oven plant or it may be the heavy tar separated in the collector main or the light tar or tarry oils separated in the condensers. The oil yield will not be the same in distilling a light tar as in distilling a total tar since there is more oil present in the former product. In other words, a light tar may be regarded as a total tar plus distillate oil and the oil yield will correspond to that from a total tar plus this additional amount of oil.

I claim:

1. Coal tar oils comprising distillate obtained by the distillation of high temperature tar to

pitch while minimizing decomposition of pitch and conducting the distillation to obtain a percentage oil yield by volume, which bears the relationship to the average melting point of the resultant pitch, in degrees Fahrenheit, such that x is equal to not less than approximately

$$87 - \frac{128}{2^{\frac{y}{100}}}$$

and not more than approximately

$$90 - \frac{128}{2^{\frac{y}{100}}}$$

in which x equals the oil yield in percent by volume and y equals the melting point of the pitch in degrees Fahrenheit.

2. Coal tar oils obtained by the distillation of high temperature tar to pitch having a melting point of at least 237° F. while minimizing decomposition of the tar undergoing distillation, resulting in the production of a percentage oil yield by volume which bears such relationship to the melting point of the resultant pitch, expressed in degrees Fahrenheit, that x is equal to not less than approximately

$$87 - \frac{128}{2^{\frac{y}{100}}}$$

in which x equals the oil yield in percent by volume and y equals the melting point of the pitch, expressed in degrees Fahrenheit and the oil yield is not more than 80 percent by weight of the tar distilled.

3. Coal tar oils comprising distillate obtained by the distillation high temperature of tar to pitch by heating the coal tar to distillation temperature while confined in and flowing through a heated zone and vaporization of the volatile oils is thereafter effected by discharging the heated tar through a chamber of low pressure relative to that of the heated zone, the tar being passed through the heated zone at an increased rate of flow amounting to not less than one-tenth of the cubical capacity of the zone per minute and heat being supplied to the tar while passing through said zone at a rate sufficient to elevate it to distillation temperature prior to its discharge therefrom, whereby the time period to which the tar is subjected to heat in its passage through the zone is diminished, thereby lowering the extent of thermal decomposition of the tar and increasing the oil yield and recovering separately the volatile oil content of the tar liberated in the vaporization chamber and the resultant pitch, the percentage oil yield by volume so recovered bearing the relationship to the melting point of the resultant pitch, expressed in degrees Fahrenheit, falling in the neighborhood of or within the limits represented by the equations

$$x = 87 - \frac{128}{2^{\frac{y}{100}}}$$

$$x = 90 - \frac{128}{2^{\frac{y}{100}}}$$

in which x equals the oil yield in percent by volume and y equals the melting point of the pitch expressed in degrees Fahrenheit.

4. Coal tar oils comprising distillate obtained

by the distillation of high temperature tar to pitch by heating the coal tar to distillation temperature while confined in and flowing through a heated tube and vaporization of the volatile oils is thereafter effected by discharging the heated tar through a chamber maintained at a pressure less than atmospheric, the tar being passed through the heated tube at an increased rate of flow amounting to not less than one-third of the cubical capacity of the tube per minute and heat being supplied to the tar while passing through said tube at a rate sufficient to elevate it to distillation temperature prior to its discharge therefrom, whereby the time period to which the tar is subjected to heat in its passage through the tube is diminished, thereby lowering the extent of thermal decomposition of the tar and increasing the oil yield and recovering separately the volatile oil content of the tar liberated in the vaporization chamber and the resultant pitch, the percentage oil yield by volume so recovered bearing the relationship to the melting point of the resultant pitch, expressed in degrees Fahrenheit, falling in the neighborhood of or within the limits represented by the equations

$$x = 87 - \frac{128}{2^{\frac{y}{100}}}$$

$$x = 90 - \frac{128}{2^{\frac{y}{100}}}$$

in which x equals the oil yield in percent by volume and y equals the melting point of the pitch expressed in degrees Fahrenheit.

5. Coal tar oils comprising distillate obtained by the distillation of high temperature tar to pitch by heating the tar to distillation temperature while confined in and flowing through a heated zone and vaporization of the volatile oils is thereafter effected by discharging the heated tar into a chamber of low pressure relative to that of said heated zone, the tar being passed through the heated zone at an increased rate of flow amounting to not less than one-tenth of the cubical capacity of the zone per minute and the heat being supplied to the tar while passing through the zone at a rate sufficient to elevate it to distillation temperature prior to its discharge therefrom, whereby the time period to which the tar is subjected to heat in its passage through the zone is diminished, thereby lowering the extent of thermal decomposition of the tar and increasing the oil yield and recovering separately the volatile oil content of the tar liberated in the vaporization chamber and the resultant pitch, the percentage oil yield by volume so recovered bearing such relationship to the melting point of the resultant pitch, expressed in degrees Fahrenheit, that x is equal to not less than

$$87 - \frac{128}{2^{\frac{y}{100}}}$$

in which x is equal to the oil yield in percentage by volume and y is equal to the melting point of the pitch in degrees Fahrenheit and the oil yield so recovered is not more than 80 per cent by weight of the tar distilled.

6. Coal tar oils comprising distillate obtained by the distillation of high temperature tar to pitch by heating the tar to distillation tempera-

ture while confined in and flowing through a heated tube and vaporization of the volatile oils is thereafter effected by discharging the heated tar into a chamber maintained at a pressure less than atmospheric, the tar being passed through the heated tube at an increased rate of flow amounting to not less than one-third of the cubical capacity of the tube per minute and the heat being supplied to the tar while passing through the tube at a rate sufficient to elevate it to distillation temperature prior to its discharge therefrom, whereby the time period to which the tar is subjected to heat in its passage through the tube is diminished, thereby lowering the extent of thermal decomposition of the tar and increasing the oil yield and recovering separately the volatile oil content of the tar liberated in the vaporization chamber and the resultant pitch, the percentage oil yield by volume so recovered bearing such relationship to the melting point of the resultant pitch, expressed in degrees Fahrenheit, that x is equal to not less than

$$87 - \frac{128}{2^{\frac{y}{100}}}$$

in which x is equal to the oil yield in percentage by volume and y is equal to the melting point of the pitch in degrees Fahrenheit and the oil yield so recovered is not more than 80 per cent by weight of the tar distilled.

7. Coal tar pitch obtained as a residue of the distillation of high temperature coal tar resulting in the production of a percentage oil yield by volume which bears such relationship to the melting point of the resultant pitch, expressed in degrees Fahrenheit, that x is equal to not less than

$$87 - \frac{128}{2^{\frac{y}{100}}}$$

in which x equals the oil yield in percentage by volume and y equals the melting point of the pitch in degrees Fahrenheit and the oil yield is not more than 80 per cent by weight of the tar distilled.

8. Coal tar pitch obtained as a residue of the distillation of high temperature coal tar while minimizing decomposition of the tar undergoing distillation and conducting the distillation to obtain a percentage oil yield by volume which bears the relationship to the melting point of the resultant pitch, expressed in degrees Fahrenheit, falling in the neighborhood of or within the limits represented by the equations

$$x = 87 - \frac{128}{2^{\frac{y}{100}}}$$

$$x = 90 - \frac{128}{2^{\frac{y}{100}}}$$

in which x equals the oil yield in percentage by volume and y equals the melting point of the pitch in degrees Fahrenheit.

9. Coal tar pitch obtained as a residue of the

distillation of high temperature coal tar wherein the tar is heated to distillation temperature while confined in and flowing through a heated zone and vaporization of the volatile oils is thereafter effected by discharging the heated tar into a chamber of low pressure relative to that of said heated zone, the tar being passed through the heated zone at an increased rate of flow amounting to not less than one-tenth of the cubical capacity of the zone per minute and the heat being supplied to the tar while passing through the zone at a rate sufficient to elevate it to distillation temperature prior to its discharge therefrom, whereby the time period to which the tar is subjected to heat in its passage through the zone is diminished, thereby lowering the extent of thermal decomposition of the tar and increasing the oil yield, the residual pitch being recovered separately from the volatile oil of the tar liberated in the vaporization chamber, the percentage oil yield by volume so recovered bearing such relationship to the melting point of the residual pitch, expressed in degrees Fahrenheit, that x is equal to not less than

$$87 - \frac{128}{2^{\frac{y}{100}}}$$

in which x is equal to the oil yield in percentage by volume and y is equal to the melting point of the pitch in degrees Fahrenheit and the oil yield so recovered is not more than 80% by weight of the tar distilled.

10. Coal tar pitch obtained as a residue of the distillation of high temperature coal tar wherein the tar is heated to distillation temperature while confined in and flowing through a heated tube and vaporization of the volatile oils is thereafter effected by discharging the heated tar into a chamber maintained at a pressure less than atmospheric, the tar being passed through the heated tube at an increased rate of flow amounting to not less than one-third of the cubical capacity of the tube per minute and the heat being supplied to the tar while passing through the tube at a rate sufficient to elevate it to distillation temperature prior to its discharge therefrom, whereby the time period to which the tar is subjected to heat in its passage through the tube is diminished, thereby lowering the extent of thermal decomposition of the tar and increasing the oil yield, the residual pitch being recovered separately from the volatile oil of the tar liberated in the vaporization chamber, the percentage oil yield by volume so recovered bearing such relationship to the melting point of the residual pitch, expressed in degrees Fahrenheit, that x is equal to not less than

$$87 - \frac{128}{2^{\frac{y}{100}}}$$

in which x is equal to the oil yield in percentage by volume and y is equal to the melting point of the pitch in degrees Fahrenheit and the oil yields so recovered is not more than 80% by weight of the tar distilled.

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