UNITED STATES PATENT OFFICE.

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METHOD OF OBTAINING ASPHALT FROM CRUDE PETROLEUM AND PETROLEUM-TAR.

SPECIFICATION forming part of Letters Patent No. 611,620, dated October 4, 1898.

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To all whom it may concern:

Be it known that we, CHAUNCEY B. FORWARD and JOHN M. DAVIDSON, citizens of the United States, residing at Cleveland, in the county of Cuyahoga and State of Ohio, have invented certain new and useful Improvements in Methods of Obtaining Asphalt from Crude Petroleum and Petroleum-Tar; and we do declare that the following is a full, clear, and exact description of the invention, which will enable others skilled in the art to which it appertains to make and use the same.

Our invention relates to a method of obtaining asphalt from crude petroleum and petroleum-tar, and also to a method of refining or reducing crude petroleum, so as to obtain asphalt as one of the results of the process.

Crude petroleum—that is, petroleum as it comes from the well—consists of a mixture of oils of various qualities from the lightest and most volatile down to the heaviest or most fixed of oils, with a black substance, which consists very largely of carbon. In this crude state the petroleum is not capable of much economic use except as a cheap fuel. The refining or reduction of crude petroleum as heretofore practiced consists in the separation of these various grades of oils from the black or carbonaceous matter, their separation from each other, and their purification. The usual process now adopted is distillation. The crude oil is subjected, under proper conditions in stills, to varying degrees of heat, and the oils pass off through the worm of the still and are then recondensed. A small degree of heat sends off the lighter oils, and as the heat is increased the various grades of heavier oils are so distilled off. The heavier the oil the greater the degree of heat necessary for its distillation off from the mass. The final residuum left after all this distillation is a hard cokey substance called "petroleum-coke," which is sometimes used for fuel and for other purposes, but which is of little value, owing to the fact that the great heat necessary to drive off the heavier oils in the process of distillation has in a great measure taken away from this substance its beneficial qualities. The distillation by which the heavier oils are driven off is a destructive distillation. It also results that during this process of distillation a considerable part of the black or carbonaceous matter is driven off with the oils—less with the lighter oils than with the heavier oils—the degree of heat to which the mass has to be subjected when the heavier oils are driven off being such as to drive off also much of the lighter or more volatile parts of the carbonaceous matter. It is necessary to treat these oils after their distillation as above described in order to purify them from this carbonaceous matter and other foreign substances.

By our improved process we take either the crude petroleum as it comes from the well or after the lighter oils have been distilled therefrom, but before the process of distillation has been carried far enough to become destructive. What is left after the lighter oils have been distilled off is known by the name of "petroleum-tar" or "residuum-oil," and we mix this in agitators or other receptacles with acid. Sulfuric acid—the oil of vitriol of commerce—is well adapted for this purpose and is cheaper than most other acids, so that we use it in preference. The quantity of acid used for a given quantity of the crude petroleum or petroleum-tar depends somewhat upon the nature of the crude petroleum or the petroleum-tar.

The crude petroleum of the Ohio and Indiana fields contains more of the carbonaceous matter than the crude petroleum of the Pennsylvania fields, and the crude petroleum from each particular field or locality differs somewhat in the relative proportion of its constituents. The more of the carbonaceous matter contained in the material treated the greater is the amount of acid required, and the petroleum-tar, containing, as it does, a greater percentage of the carbonaceous matter than the crude petroleum itself before the lighter oils have been taken off, requires a larger percentage of acid than the crude petroleum from which it is derived, and the more oil that has been taken off the greater the percentage of the carbonaceous matter in the tar or residuum will be and the greater the

amount of acid required. It is not necessary to regulate the amount of acid used with any great degree of nicety, because the acid is inexpensive and most of it is afterward recovered back, and the use of more than is necessary within limits does no harm. It is best to regulate the quantity used by experiment with the particular material or residuum under treatment, being sure to use enough. Generally speaking, the amount of acid will vary from eight per cent. to twenty per cent. of the amount of the crude petroleum or petroleum-tar under treatment, eight per cent. or fourteen per cent. being sufficient when ordinary crude petroleum is being treated and from twelve per cent. to twenty per cent. being required for the best effect when the petroleum-tar is being treated. It will rarely, if ever, be found necessary to use more than twenty per cent. It is easy, by a little experience in the particular material under treatment, to regulate the percentage of acid which it is best to use. The material is then heated in the agitators and thoroughly agitated. If the crude petroleum as it comes from the well is under treatment, the heat should not exceed about 80°, else a considerable part of the lighter oils will pass off in vapor. If the petroleum-tar is being treated, the heat may be as high as 100° or 110° without injury. In treating the crude oil we prefer to take off by distillation some, at least, of the lighter oils first, because it enables us to use a greater degree of heat in the agitating process and the results are more satisfactory. After this material in the agitators has been so heated and agitated it is allowed to settle. It will be found that the acid has united with the carbonaceous matter, and as the material in the agitators settles this combination of the carbonaceous matter and the acid is precipitated to the bottom, and it or the clear material above may be drawn off and thus the oils separated from the carbonaceous matter. The oils so freed from the carbonaceous matter which was before contained in them should be thoroughly washed, so as to remove any remaining acid therefrom. The process of washing is well known. The material to be washed is thoroughly mixed with alkaline water—it is better to be hot—and then, upon settling, the oil rises to the top and the water carrying the acid sinks to the bottom. The oil may be drawn off from the top of the tank or agitator and the water containing the acid drawn off from the bottom, and thus they are separated. The acid may be then separated from the water and saved by a process of distillation which is well understood. We have now remaining the carbonaceous matter, previously contained in the crude petroleum or the petroleum-tar, mixed with the greater portion of the acid which has been used in the treatment. It is from this substance that the asphalt or bituminous product is made. We first wash it to separate the acid therefrom. The process of washing this is similar to that employed in washing the oil, and the result is that the water containing the acid sinks to the bottom and the carbonaceous matter, substantially clear of the acid, rises to the top, and the carbonaceous matter may be drawn off from the top or the water from the bottom and so separated. This acid can be recovered from this water by the same process of distillation as before mentioned. It is usually best to repeat this washing process two or three times in order to more thoroughly remove the acid from the carbonaceous matter. Most of the acid will be recovered in the first washing; but some of it will always remain to be taken out by a second and third washing, and its presence in the carbonaceous matter in any considerable amount is injurious. We now have the carbonaceous matter which was originally in the crude petroleum or petroleum-tar with the oil and the acid removed. Some portion of the oil will adhere to the carbonaceous matter, and its presence is beneficial rather than otherwise and some traces of the acid may remain; but if the washing has been thorough there will not be enough to do any harm. This material by itself will not make the best grades of asphalt. It contains too large a proportion of volatile matter. For the best result it is necessary to mix it with some heavy oil. The heavy hydrocarbon oil, one of the well-known products of any system of petroleum-refining, answers this purpose very well and is very cheap. Under our process such oil will be produced from the mixture of oils which remains after the carbonaceous matter has been separated therefrom by the acid treatment, being the product remaining in the still after all lighter oils have been separated from said mixture by distillation, and under the treatment heretofore employed in petroleum-refining it will be produced as the last product of distillation. The heavier the oil the better, and it makes no difference whether or not it has been treated so as to purify it. All that is necessary is that it should be a very heavy oil, and such oil as we need is quite inexpensive.

The proportion of heavy oil to the carbonaceous matter may vary according to the character of the material to be mixed with it and of the product required, as will be hereinafter more particularly explained. This heavy oil and the carbonaceous matter are then thoroughly mixed. The mixture may be effected by any mechanical means adapted to the purpose. The mixture is then subjected to a high degree of heat, preferably as high as 800° Fahrenheit. This heat should be kept up for from four to eight hours. During the heating such mechanical changes or chemical reactions take place as to convert the combined material into a superior grade of asphalt, and the process may in some cases be terminated at this stage; but for many purposes the asphalt is improved and the products made cheaper by the addition to it

of a proportion of marl. The marl is introduced after the heating process and before the substance cools and becomes hard.

In the mixture of the heavy oil and the carbonaceous matter we prefer about twenty-five per cent. of the oil to seventy-five per cent. of the carbonaceous matter; but these proportions may vary. The carbonaceous matter is not always of exactly the same constituency. That obtained from one oil-field will differ from that obtained from another, and the carbonaceous matter obtained from the petroleum-tar after the lighter oils have been distilled away is a little different from that obtained from the crude petroleum, for the reason that in the distillation of the lighter oils some of the more volatile parts of the carbonaceous matter have been distilled away with them, and its character varies somewhat according to the amount of acid employed and the care with which it has been removed, as well as the thoroughness with which the separation between the oil and the carbonaceous matter has been effected. The percentage of heavy oil to carbonaceous matter also depends in some degree upon the character of the oil employed. The heavier the oil the less of it is necessary, because it is the heaviest part of the oil that produces the beneficial result. Exactitude in the percentage between the oil and the carbonaceous matter is not necessary. Generally speaking, the heavier the carbonaceous matter is—that is, the more its more volatile portions have been removed—the more oil should be used, and the more elastic and pliable the manufacturer desires the asphalt to be the more heavy oil should be used. The proportion of twenty-five per cent. of oil to seventy-five per cent. of carbonaceous matter will always produce an asphalt of high grade, and it will not be found necessary to vary in any considerable degree from these percentages.

The degree of the heat to which the mixture of the carbonaceous matter and the heavy oil is subjected and the length of time to which it is subjected to that heat also depend somewhat upon the character of the material used and of the result required. The heat should be continued long enough to effect the desired change in the substances. A good test of whether or not sufficient heat has been employed is to take out a sample of the substance and subject it to the action of water. If the heat has been employed long enough, water will not disintegrate it. If not, it will. After the heating process has been continued for the proper length of time one can handle it as he can chewing-gum, and one may chew it like chewing-gum without any disagreeable results. It will be easy in this way to determine when the heating process is complete.

The quantity of marl used will depend upon the character of the asphalt required and the purpose for which it is to be used. The marl gives it weight, body, consistency, and tensile strength. For asphalt designed for ordinary street-paving it will be found advisable to add about twenty per cent. of marl. For some purposes as much as thirty per cent., or even a very much higher percentage may be added. A mixture of marl and the asphalt as it is produced at the end of the heating process in the ratio of about three parts of marl to one part of the asphalt makes a most excellent and durable paving-brick.

For a cheaper grade of asphalt the heavy oil may be entirely omitted. In this case the carbonaceous matter should be subjected to the same treatment by heat as we have described for the mixture of the carbonaceous matter and the heavy oil, except that it cannot be subjected to as high a degree of heat, because that degree of heat would be destructive of the substance if the oil was omitted. 600° Fahrenheit would be as high a degree of heat as it would be safe to employ without the oil. If marl is added, it should be at the close of the heating process in the same way as we have described when the heavy oil is used. If the oil has been omitted, the marl may be used more freely, because the product will be of a cheaper grade any way, and more marl may be used without depreciating the quality of the result.

Marl is mostly carbonate of lime, and lime in any other form may be used instead of marl, but the cheapness of marl makes its use preferable, and its use gives the best results.

What we claim is—

1. The process of making asphalt from crude petroleum by treating the crude petroleum with acid to separate the carbonaceous matter from the oils, washing the carbonaceous matter to free it from the acid, then mixing it with heavy hydrocarbon oil and subjecting it to a high degree of heat for a considerable period, substantially as described.

2. The process of making asphalt from petroleum-tar or from crude petroleum after the lighter oils have been distilled off by treating it with acid to separate the carbonaceous matter from the remaining oils, washing the carbonaceous matter to remove the acid, then mixing it with heavy hydrocarbon oil and subjecting the mixture to a high degree of heat for a considerable period, substantially as described.

3. The process of refining or reducing crude petroleum by treating it with acid to separate the mixture of oils obtained by this process into oils of various kinds by successive distillations, by mixing the carbonaceous matter separated as above from the oils with heavy hydrocarbon oil and subjecting the mixture to a high degree of heat for a considerable period, substantially as described.

4. The process of making asphalt from crude petroleum by first treating the crude petroleum with acid to separate the carbonaceous matter from the oils, then adding to

said carbonaceous matter a heavy hydrocarbon oil and subjecting the same to a high degree of heat, and then adding marl or lime, substantially as described.

5. The process of treating petroleum-tar or petroleum after the lighter oils have been removed by distillation, by using acid to separate the carbonaceous matter from the remaining oils, by mixing the same with a heavy hydrocarbon oil and subjecting the mixture to a high degree of heat and then adding marl or lime, substantially as described.

6. The process of producing asphalt from crude petroleum or petroleum-tar by treating the same with acid to separate the carbonaceous matter from the oils, then subjecting this carbonaceous matter to a considerable degree of heat for a considerable period, substantially as described.

7. The process of producing asphalt from crude petroleum or petroleum-tar by treating the same with acid to separate the carbonaceous matter from the oils, then subjecting this carbonaceous matter to a considerable degree of heat for a considerable period and then adding marl or lime, substantially as described.

Witness our hands to the foregoing specification.

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