No. 635,430. Patented Oct. 24, 1899.

G. F. & G. C. K. CULMER.

ASPHALTIC FLUX.

(Application filed Sept. 21, 1899.)

(No Model.)

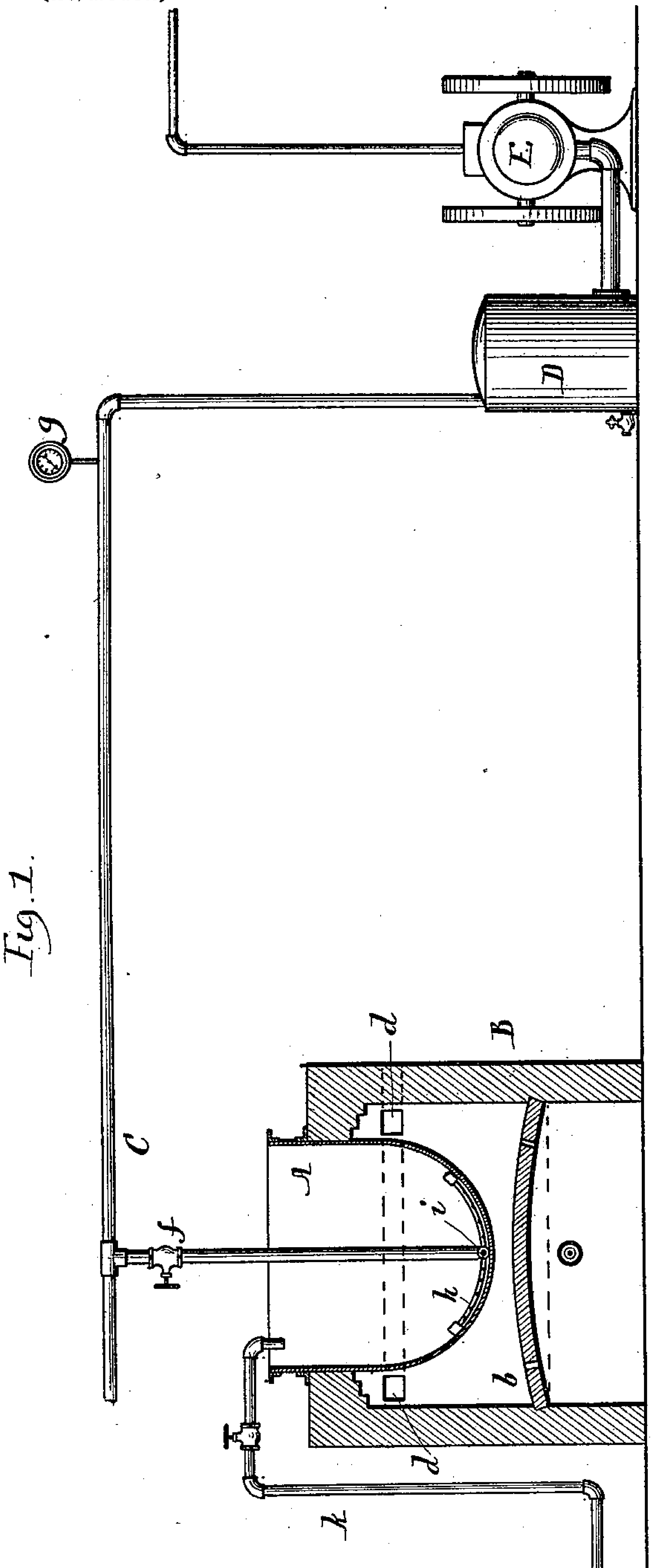

Fig. 1.

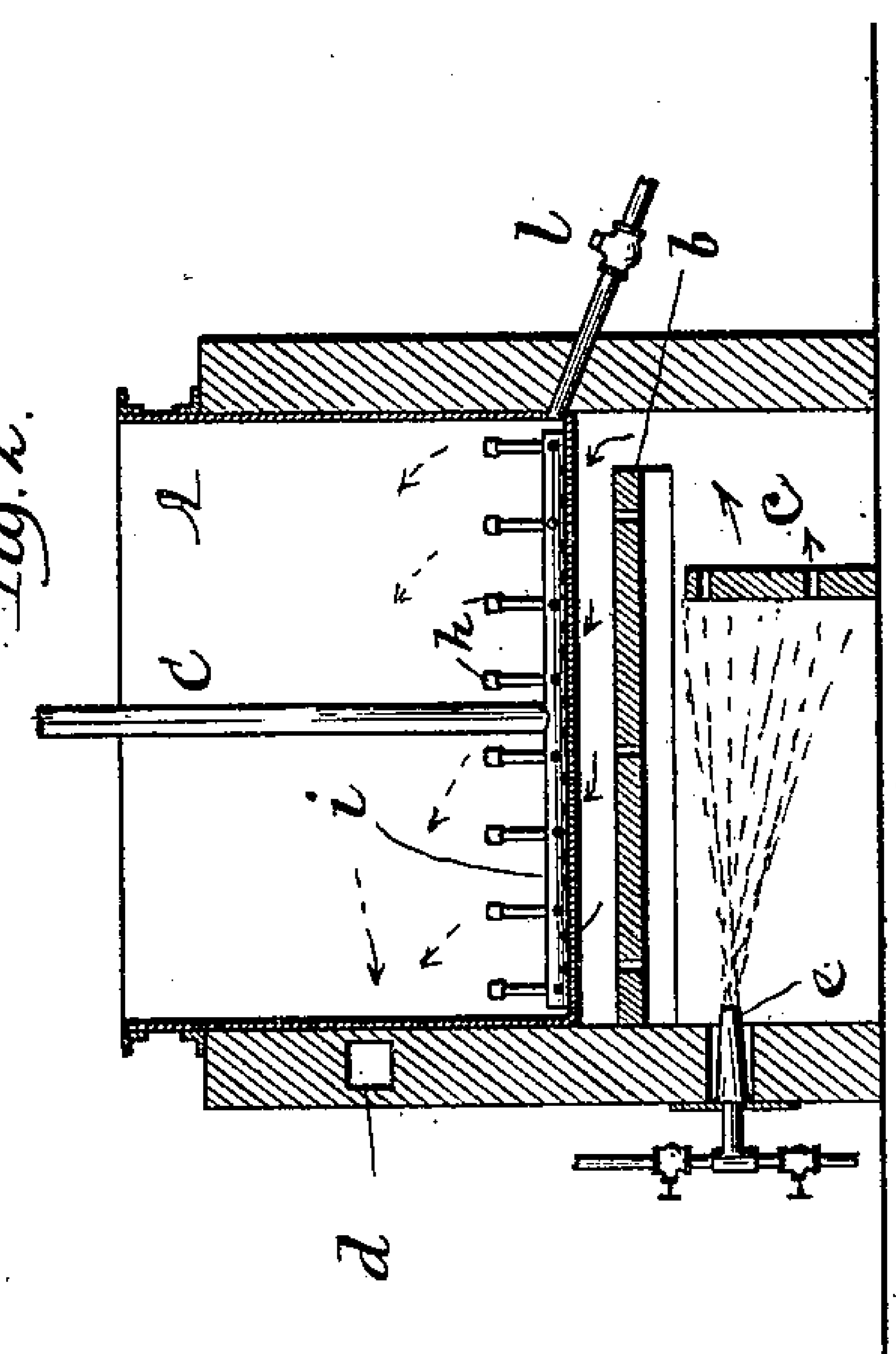

Fig. 2.

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UNITED STATES PATENT OFFICE.

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ASPHALTIC FLUX.

SPECIFICATION forming part of Letters Patent No. 635,430, dated October 24, 1899.

Original application filed February 21, 1898, Serial No. 671,084. Divided and this application filed September 21, 1899. Serial No. 731,156. (No specimens.)

To all whom it may concern:

Be it known that we, GEORGE F. CULMER and GEORGE C. K. CULMER, residents of Chicago, Illinois, have invented certain new and useful Improvements in Asphaltic Fluxes, of which the following is hereby declared to be a full, clear, and exact description.

In the preparation of asphaltic cements—such, for example, as are employed in paving or for roofing or other purposes—it is familiar practice to admix, say, eighty per cent. of refined Trinidad asphalt with twenty per cent. of the oil residuum from petroleum distillation. The residuum is heated to 250° to 300° Fahrenheit and the refined asphalt added thereto, melting gradually in the menstruum. The mixture is maintained at the stated temperature for some six to eight hours, during which period air is injected into the mass in various quantity, chiefly as an aid for disengaging the bitumen present from its intimate association with the earthy sediments retained thereby and as well to insure the intimate admixture of the refined asphalt with the added residuum. Incidentally the air injected acts to drive off the water and such minor portion of the hydrocarbons as may freely volatilize under the prescribed conditions. At the end of the treatment the residuum has become thoroughly amalgamated with the refined asphalt, producing a homogeneous compound, into which pulverized limestone and sand can be admixed, as in usual preparation of paving materials. The residuum serves, in a sense, as a solvent for the refined asphalt, markedly reducing its hardness, but by reason of the low melting-point of the resultant compound exposing it always to the risk of "flow" under heat of the summer sun. Any material excess in the percentage quantity of the residuum taken still further lowers the melting-point of the final compound. Practically twenty per cent. of residuum additional is about as much as the refined asphalt can absorb and yet afford an ultimate product acceptable for paving purposes.

The present invention designs to profoundly modify the character of the petroleum residuum, the course of treatment being so far radical that a flux is obtained not differing very widely in specific gravity or volume from the original residuum, but highly distinctive in its value as an agent to "cut" refined Trinidad asphalt and other materials, as hereinafter specified.

With Trinidad asphalt, for example, the improved flux can be used, say, to the extent of sixty to eighty per cent. to afford a paving composition at once firm and elastic in winter without being brittle, nor yet liable to flow on exposure to the summer sun. The cost of the compound is decidedly cheaper by reason of the lessened quantity of refined asphalt taken, this being displaced to advantage by the large increase of the flux addition at notable saving in expense.

For the practice of the invention residuum of 18° to 22° Baumé, derived on "cracking" crude petroleum, is a convenient source of primary supply. Residuum from the Lima, Ohio, oil district serves the purpose very well.

In ordinary course fractional distillation of petroleum advances through successive stages until the paraffin and heavy lubricating vapors are driven off under partial vacuum at about 550° to 600° Fahrenheit. Residuum is the liquid remnant yet retained in the still. Residuum often varies in density between the limits above noted, especially if steam be used to clarify it. Protracted air exposure also increases the quantity of water present therein.

An advantageous mode of procedure suited for the production of the improved flux will next be set forth in detail. Modifications in such procedure may occur according to the skill of the mechanic without material change in the characteristics of the resultant flux. Some of these modifications will be outlined.

On the drawings which accompany, Figure 1 is a view in cross-section, exhibiting a form of kettle suited for production of the desired flux. The compression-pump, reservoir, and service-pipe supplying air to the kettle are displayed in elevation. Fig. 2 is a view of the kettle at cross-section to Fig. 1.

The kettle A to contain the charge may be one of a series of like vessels. As here shown, the kettle is preferably made of boiler-plate or other stout metal. It is somewhat oblong with rounded bottom and depends from the crown of a furnace B. A simple arch *b*, with bridge *c*, directs the course of the furnace flame beneath and around the kettle into the exit-flue *d*, leading to the chimney. By aid of the atomizing-jet *e* hydrocarbon fuel can be used to furnish the requisite heat. The jet can be turned on or off at will, as may seem requisite, the amount of external heat, if any, applied being thus within easy control of the operator.

Service-pipe C for the air-supply is furnished with usual cock *f* and gage *g*. It leads from the equalizing-reservoir D, connected with compression-pump E, and at its opposite end is submerged in the kettle, terminating in a series of perforated branches *h*, which unite with the central trunk *i* and serve to distribute the air evenly throughout the kettle in near relation to its bottom. The charge of residuum is delivered to the kettle by tube *k* and the finished batch withdrawn therefrom through exit-tube *l*.

While the device here shown is economic and efficient in use, it is obvious that other kinds of apparatus can be employed or the details be varied as the skill of the mechanic may suggest.

Let ten hundred and fifty gallons (say seven thousand seven hundred and seventy-seven pounds) of petroleum residuum at about 18° Baumé be run into an open kettle loosely covered by a hood of size sufficient to catch the escaping vapors and deliver them to a suitable exit. The kettle is heated by direct fire. When the temperature of the residuum attains, *e. g.*, 380° Fahrenheit, which may require some eight hours' heating to effect, the batch can be advantageously held at such point during treatment. While this preliminary heating is in progress, the residuum expands in the kettle and foams markedly, giving off a notable quantity of what for the most part are watery vapors. Gradually the batch becomes quiescent and at 380° Fahrenheit may have lost some four hundred pounds in weight. No material change in the qualities of the residuum has occurred, and the same would be true were the mere heating of the batch continued, say, for thirty-two hours additional. This sort of negative result might be expected, inasmuch as the residuum stands as a remnant left substantially unaffected in the still at much higher temperature. Into the hot quiescent batch at 380° Fahrenheit air is now injected by perforated pipe suitably branched and located near the kettle-bottom to evenly distribute the oxidizing agent throughout the liquid. The air-pipe is connected externally with a force-pump or other source of supply. Treatment by air-blast may extend over a period, *e. g.*, of forty hours, divided roughly into a first stage of about thirty-two hours' duration and a second or final stage for some eight hours more. The volume of air injected varies as the treatment proceeds, the inflow per hour ranging from six thousand five hundred to five thousand cubic feet during the first stage and from four thousand to three thousand cubic feet during the second. Under influence of the air the batch gradually thickens, its notable progress in such regard marking the close of the first stage. Eventually the operator is obliged to lessen the blast. An increase in the internal heat of the batch is also observed. To maintain the mass at even temperature—*e. g.*, 380° Fahrenheit—as may often prove desirable, the air-blast can be diminished temporarily at times, although it suffices generally to check the fire instead. At the close of a forty-hour run, during which the batch at 380° Fahrenheit has been exposed to the action of the air, the batch will have lost some 3.5 to four per cent. by weight. Evaporation is thus seen to be comparatively slight. The characteristics of the finished flux are to be attributed rather to changes of a chemical sort occurring within the mass.

By means of a Soxhelt extraction apparatus bituminous substances may be digested with (*a*) petroleum ether—*e. g.*, gasolene boiling at 70° to 80° centigrade—and the residue be later digested with (*b*) carbon disulphid, which is a solvent for the bitumen proper, but leaves some of the associated organic materials and the inorganic or mineral constituents unaffected. The ingredients soluble in petroleum ether are conveniently termed "petrolene," while that part of the residue dissolved by carbon disulphid is called "asphaltene." The percentage of asphaltene in its relation to the total weight of the sample first taken can be readily calculated. This mode of analysis is a convenient guide for the ready display of the successive transformations which the batch experiences in course of treatment according to the method detailed herein and affords a clue to the inherent results characteristic of such treatment.

The comparative table next following displays the changes in content (notably of petrolene and asphaltene) which transpire in practice, as exemplified by actual test of samples taken at the beginning of the air-injection and at various hours thereafter:

	Hours.			
	0.	16.	32.	40.
Petrolene	------	90.51	74.41	73.34
Asphaltene	2.50	8.03	23.46	25.14
Other organics	------	0.85	1.40	0.89
Mineral	------	0.61	0.70	0.63
Total	------	100.00	100.00	100.00

The residuum loses in petrolene, but gains in asphaltene, and it is this marked change in composition which enables the finished product to perform the functions of a flux. The higher its per cent. of asphaltene the higher will be the melting-point of the resultant mixture obtained should the flux be applied as an agent to cut rich bitumens, such as gilsonite, wurtzilite, uintahite, &c., or the poorer sorts, such as refined Trinidad asphalt.

The details given thus far relate, as was stated, to a sample batch or residuum. Its approximate weight in the crude was seven thousand seven hundred and seventy-seven pounds. At the outset of the air treatment on reaching 380° Fahrenheit after eight hours' heating the weight was seven thousand three hundred and eighty-seven pounds and at the close of the treatment forty hours later was some seven thousand one hundred and three pounds. For the first thirty-two hours of the blasting operation the average air-supply per minute was about one hundred cubic feet to the one thousand gallons. If the flux thus derived be accepted for convenience of comparison as a "standard" grade, it is plain that on holding the temperature beyond 380° Fahrenheit a harder flux will be produced and below such temperature a softer. Hence at the higher range the air-blast need be used for less time to afford a standard yield. At the lower range the blast must persist longer; or, again, at the lower range, for example, by increasing the volume of air-supply the period of treatment is lessened. Doubling the blast may nearly halve the time.

As the foregoing table shows, the thirty-two-hour flux differs markedly from the sixteen-hour variety, but more closely resembles the forty-hour sort. In many instances the thirty-two-hour flux is on the whole to be preferred. An increase of temperature and of air volume during the blast may easily reduce the period of treatment necessary to obtain such quality of flux, say, to sixteen hours. Nor is it requisite to hold the batch at even temperature during the blast, although the results are more certain, especially at the hands of unskilled workmen, if this occurs. Indeed, the blast can be turned on before the batch has attained the desired degree of heat; but this must be at the risk of undue "foaming," particularly in the earlier stages.

When the flux is to be prepared as a separate market product capable of a variety of uses, the residuum can be treated alone. Yet it is entirely feasible to combine therewith refined Trinidad asphalt—for example, say fifty per cent. of each—and carry this mixture through the preliminary heating and through the air-blast treatment beyond when the purpose is to obtain a pavement composition suited for union with limestone powder and sand, as in usual practice; but such procedure demands larger kettles or boilers and is more cumbrous. Certainly the high per cent. of residuum present will enable the Trinidad asphalt to more quickly scour itself free from the associated earthy sediments. While the air-blast stirs the mass to aid the scouring, yet when the air is shut off to clear the liquid of the sediments this must be at risk of "scorching" the asphalt which lies nearest the walls of the kettle unless the heat be comparatively low. Once the sediments are cleared the temperature can be raised and the air be injected in proper volume suited for the formation of the flux the same as if no asphalt were present. The period of oxidizing treatment may extend over sixteen to thirty-two hours, dependent upon conditions already stated. On the whole it is better to prepare the flux separately in avoidance of the complexities and possible injuries which the asphalt ingredient may incur.

Heavy crude oils, such as are found in California, and other like natural oils may be used without preliminary distillation as a substitute for the residuum. The air-blasting will proceed under much the same conditions; but the escape of watery and light oil vapors will entail a much larger flow in the weight of the derived flux than if residuum were employed.

With the temperature constant it is obvious that the longer the air treatment persists the higher becomes the asphaltene content of the flux, and in consequence the higher its melting-point. Variations occur in keeping with the uses to which the output is to be applied.

Fluxes produced by blowing the batch for a given number of hours—say at 380° Fahrenheit—will impart a medium melting-point to the final compound obtained on admixture of the resultant flux with the selected base. If the flux be derived, *e. g.*, at 300° Fahrenheit, the melting-point becomes relatively low. On the contrary, if the batch be blown at higher degree—*e. g.*, 450° Fahrenheit the melting-point is also advanced. Working at 450° Fahrenheit demands an increased injection of air, particularly if continued for any considerable period, the object being to detain in an oxidized state such of the constituents as might otherwise pass off in material diminution of the volume of the batch. Should the heat be excessive, the mass will destructively distil, losing perhaps one-half of its weight and leaving a pitch behind. All such excess is to be avoided.

Asphaltic fluxes made in keeping with the invention are black and semisolid at ordinary temperatures. Under sufficient heat they fuse readily to a limpid liquid. After dehydration—*i. e.*, after expulsion of the water generally present as an adulterant of the market article—the primary petroleum residuum varies but slightly in specific gravity from the derived flux, the notable differences between them appearing instead by the remarkable change in the relative content of asphaltene and petrolene, respectively. These changes are to be attributed to the air-blast treatment. As a consequence the flux can be admixed with the selected base in far greater quantity and still establish a melting-point for the compound even higher than if a minor quantity of crude residuum were taken instead. For the preparation of pavement compositions this characteristic of the flux is of significant value; but it has other important uses besides. For instance, uintahite is a native mineral consisting of nearly pure bitumen. Its melting-point is about 244° Fahrenheit. Adding fifty per cent. uintahite to fifty per cent. of hot liquid asphaltic flux which has been subjected to air-blast, say, for forty hours produces a compound melting at 260° Fahrenheit and capable of excellent use for lining the sides and bottoms of water-reservoirs. Uintahite, thirty per cent., and seventy per cent. asphaltic flux derived by air-blast treatment at 380° Fahrenheit for twenty-four hours affords a roofing compound melting at 170° to 190° Fahrenheit. Uintahite, thirty per cent., with seventy per cent. of asphaltic flux derived by air-blast treatment at 500° Fahrenheit for seventy-two hours, yields a dip suitable for coating iron or other metal pipes, the dip melting at about 270° Fahrenheit and being used as a bath in the usual tank at, *e. g.*, 400° to 450° Fahrenheit.

Examples like the foregoing display the wide range of use for these asphaltic fluxes under varying conditions and exhibit the relatively high per cent. of the flux which can be safely taken at low cost to utilize the valuable qualities of the pure bitumen. The fluxes are of equal advantage in dealing with other sorts of bituminous base, whether native or artificial, and in melted state can act as a solvent to cut gilsonite, elaterite, wurtzilite, and asphalt or analogous gums.

It is impracticable to multiply formulæ. The skill of the mechanic under sample tests taken, as usual, in course of compounding will generally afford sufficient guide. The base to be cut can be added in the flux-kettle while blasting proceeds, or, better yet, at the close of the air treatment or on reheating the flux at some subsequent occasion. Several sorts of base can be admixed at once with the same flux.

The process hereinbefore set forth is made the subject of a separate application filed February 21, 1898, Serial No. 671,084. The present case is a division thereof and is restricted to the product—*i. e.*, to the asphaltic fluxes—obtained by practice of such process, which latter is not claimed herein.

Having thus described our invention, what we claim as new, and desire to secure by Letters Patent, is—

A black semisolid asphaltic flux devoid of pitch the same consisting of dehydrated and oxidized petroleum residuum nearly alike in volume and specific gravity, with the original residuum but markedly higher in its content of asphaltene and lower in its petrolene than the residuum from which it was derived and possessing the characteristics of a product obtained by prolonged exposure of petroleum residuum to a heat below pitch-forming temperature *e. g.*, below 550° Fahrenheit, under copious injection of air to transform the mass without material distillation, substantially as described.

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