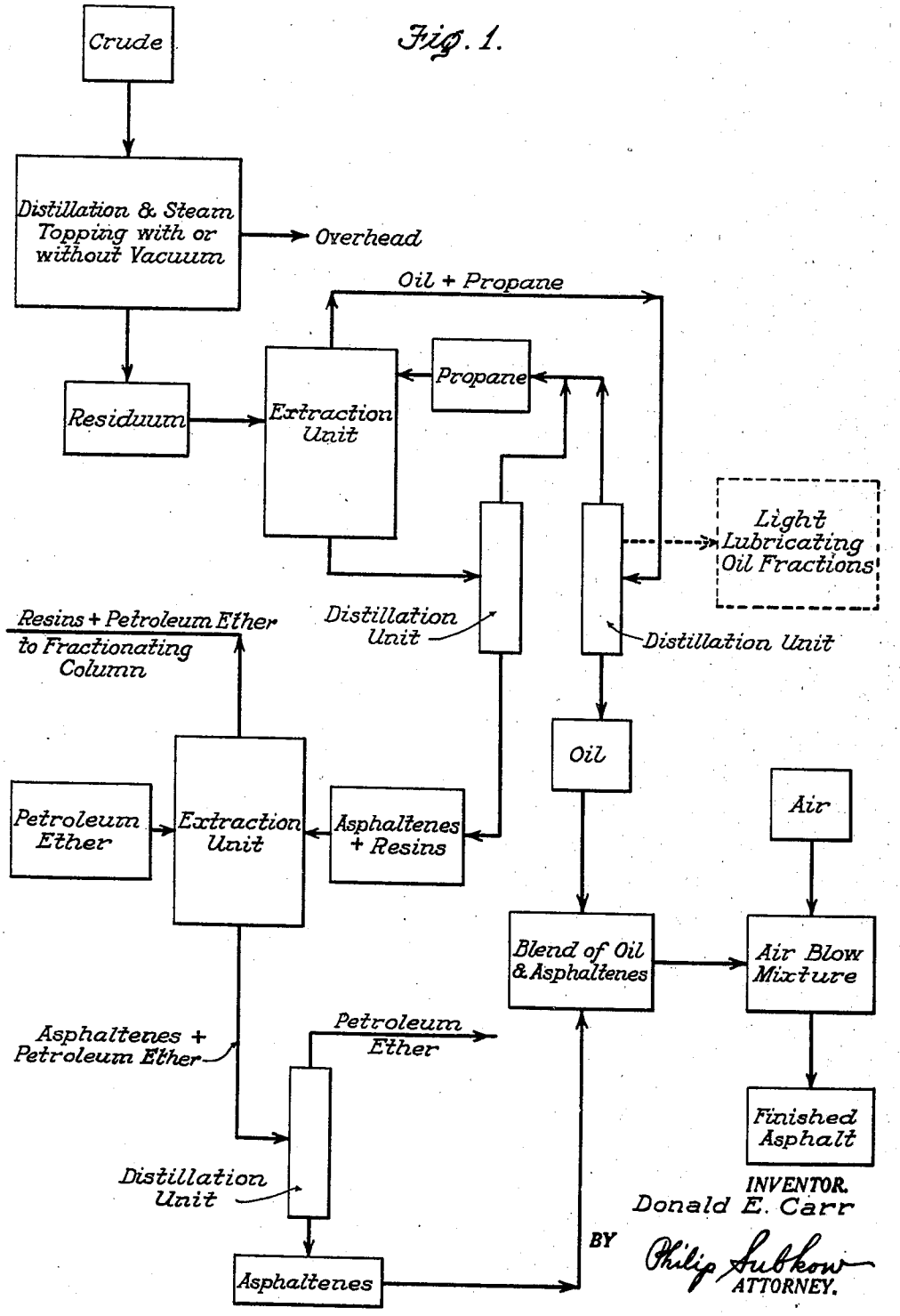
March 10, 1942. D. E. CARR 2,276,155

ASPHALT AND PROCESS FOR PRODUCING THE SAME

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Fig. 1.



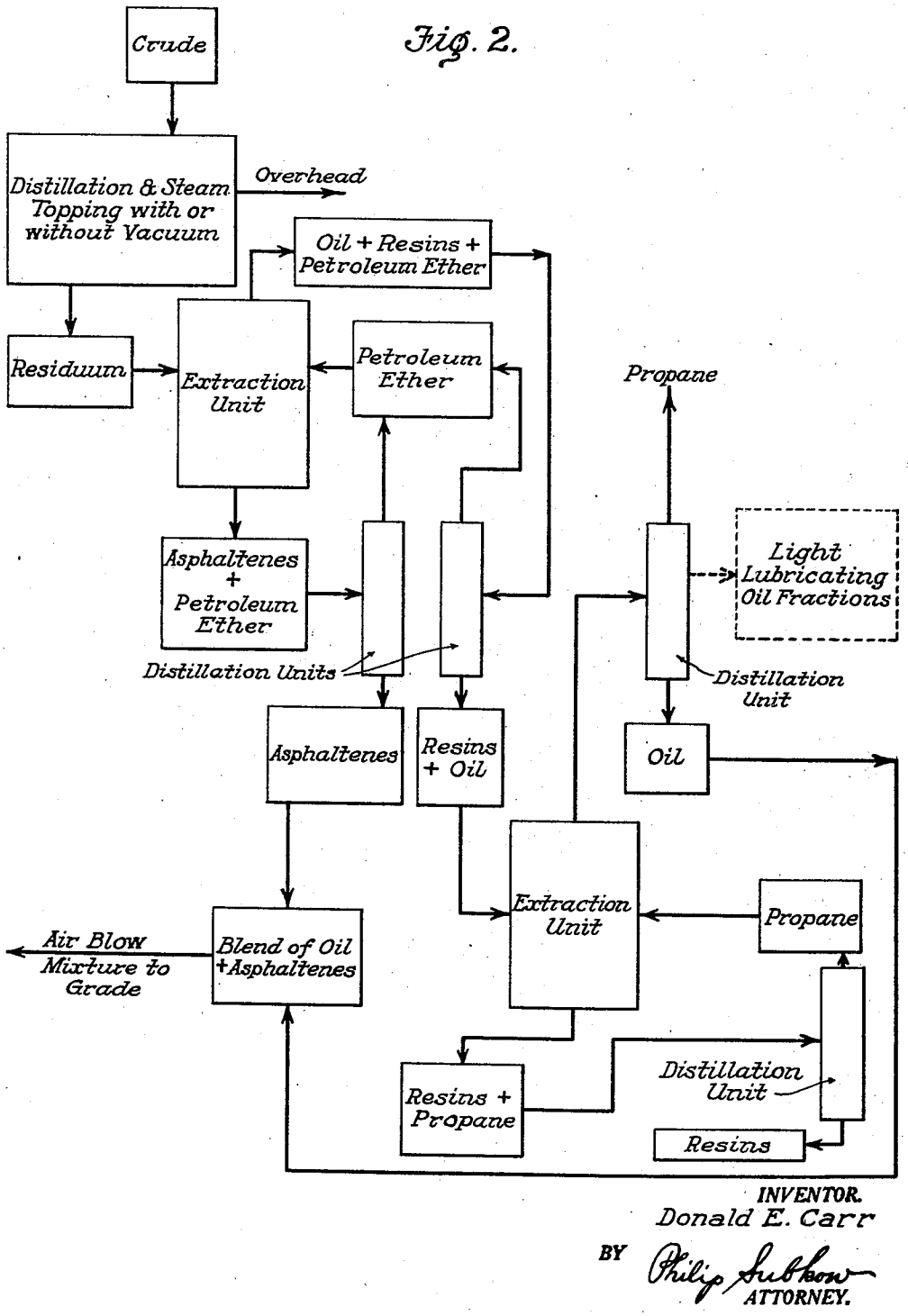
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Fig. 2.



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Patented Mar. 10, 1942

2,276,155

UNITED STATES PATENT OFFICE

2,276,155

ASPHALT AND PROCESS FOR PRODUCING THE SAME

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Application February 7, 1939, Serial No. 255,084

9 Claims. (Cl. 196—74)

This invention relates to a process for the manufacture of asphalts, particularly air-blown or oxidized asphalts.

It is an object of my invention to improve the air-blown characteristics of asphalts and their stability to weathering.

It is another object of my invention to improve the characteristics of the charging stock from which the oxidized asphalt is produced. Other objects of my invention will appear from the following description.

It is well known in the art of manufacturing air-blown asphalts that such products may be prepared by blowing the charging stock with air or other oxygen containing gases at an elevated temperature and that the resulting oxidized asphalt will possess desirable low temperature susceptibilities, high melting point for given penetration and moderately high ductilities. The charging stock generally employed is a topped residuum obtained from an asphalt base crude oil.

It is generally recognized in the asphalt industry that the nature of the charging stock used in the manufacture of air-blown asphalt has a very marked effect on the properties of the air-blown product. Some charging stocks produced from certain selected crude oils oxidize to better asphalts than charging stocks produced from other crude oils.

Heretofore, very little was known concerning the nature of the reactions occurring during the blowing process of what factors were responsible for the high or low quality of the resultant air-blown products. I have now discovered that by means of proper solvent fractionation, asphaltic materials may be separated into three components, namely, asphaltenes, resins and oil. In this specification the term "asphaltenes" is defined as those components of topped residuum which are insoluble in propane and insoluble in petroleum ether. The term "resins" includes those constituents of topped residuum which are insoluble in propane but soluble in petroleum ether. "Oil" comprises those materials present in topped residuum which are soluble in both propane and petroleum ether. By the term "topped residuum" is meant those materials derived from crude oil by the removal of the more volatile fractions up to and including at least the gas oil fraction thereof. A portion of the lubricating oil may also be removed by distillation. Furthermore, it is intended to include those naturally occurring asphaltic materials, such as Trinidad asphalt.

I have discovered that during the air-blowing process for producing oxidized asphalts from residua the oil fraction of the asphalt remains substantially unchanged in amount except for distillation losses but that the proportion of the resin fraction decreases progressively as the length of air-blowing increases, the resins apparently being polymerized to form materials of the class of asphaltenes and that consequently the proportion of asphaltenes in the finished product is increased over that present in the residuum prior to air-blowing. Furthermore, I have discovered that the asphaltene fractions of various residuum are relatively stable to weathering whereas the resins and particularly the lighter resins are relatively unstable to weathering and tend to form oxidation products upon exposure to light in the presence of oxygen. It has already been determined that the lighter lubricating oil fractions also give rise to instability of air blown asphaltic materials but that the relatively heavy lubricating oil fractions are similar to the asphaltenes insofar as stability to weathering is concerned.

As the result of the above discoveries I have been able to produce a synthetic asphaltic residuum which can be oxidized in a fraction of the time heretofore required for naturally occurring residuums to produce air-blown asphalts of unusually high stability as regards weathering. These desirable objects are accomplished by separating the asphalt into fractions comprising asphaltenes, resins and oil and subsequently blending the oil with the asphaltenes in desirable proportions to yield an air-blowing stock already possessing mildly air-blown characteristics which are improved to any desired extent by only a short period of oxidation with air or other oxygen containing gas. By this process it will be noted that the resin fraction, which represents the unstable portion of asphaltic material, and the conversion of which to asphaltenes represents the time consuming process in the air-blowing of naturally occurring residua has been eliminated. In practicing this invention I have found it desirable to conduct the separation of asphaltenes from the residuum in such a manner that a portion of the heavier more stable resins are separated with the asphaltenes in order to act as plasticizers for the latter material in order that it may be subsequently more readily admixed with the oil fraction separated from the residuum.

In general, the separation of the charging stock into asphaltenes, resins and oil may be accomplished in a number of ways. According to one method, the asphalt residuum may be first extracted with a solvent adapted to disssolve all of the oil and to precipitate substantially all of the asphaltenes and resins. The precipitate is then extracted with a solvent adapted to dissolve substantially all of the resins and to precipitate all of the asphaltenes. The asphaltenes and the oil may then be blended in the desired proportion to produce a composited asphalt

which may be oxidized to the desired characteristics.

In another method, the asphalt residuum may be first extracted with a solvent adapted to dissolve substantially all of the oil and resins and to precipitate all of the asphaltenes as a resin free fraction. The oil and resin mixture may then be extracted with a solvent adapted to dissolve substantially all of the oil and to precipitate the resins. Again the asphaltenes and the oil may be blended in the desired proportion to produce the composited asphalt which then may be further oxidized to the desired characteristics.

The process may be better understood by reference to the drawings which represent schematic flow sheets for carrying out the process. According to Fig. 1 of the drawings, an asphalt-containing crude oil is first distilled and steam topped with or without vacuum to distill at least all of its gas-oil content. The still bottoms or the asphalt residuum is then extracted with a solvent which is adapted to dissolve substantially all of the oil but which will precipitate all of the asphaltenes and resins. Solvents capable of effecting this separation are the liquefied normally gaseous hydrocarbons such as ethane, propane, butane, iso-butane, and sometimes pentane, or mixtures thereof. Such hydrocarbons are obtained by rectification of casinghead gasoline by the so-called stabilizing method now conventional in the natural gasoline industry. They comprise the overhead gaseous fractions of the stabilizing process. The gaseous fractions are liquefied by compression and cooling in the conventional manner and are drawn off into pressure chambers where they are maintained in the liquid state until they are used. The necessary pressure to maintain propane, for example, in a liquid state, is approximately 125 lbs. per square inch at about 75° F. Of course, the extractive power of the solvent may be varied by varying the conditions of extraction, for example, the temperature of extraction and the amount of solvent. In the drawings, I have shown the extraction of the oil from the asphaltenes and resins as being carried out with the use of propane. In this case, the residuum is mixed with about 3 to 6 volumes of propane at a pressure of about 125 lbs. or upwards, preferably at a temperature of 100° F. and the mixture is allowed to remain in a quiescent state until the precipitated asphalt and resins have settled to the bottom of the container. The clear supernatant solution of oil and propane substantially free from resins is then decanted and subjected to distillation to remove the propane which may be recovered by compression and cooling and returned for further treatment of residuum. Depending upon the degree of topping of the crude oil, the oil may at this point be fractionally distilled to remove light lubricating oils since the volatility of an asphalt essentially determines its weathering durability or storage stability. The evaporation of oils from asphalt over a period of time results in embrittlement, cracking, checking, etc. However, these oils may be removed in the initial topping of the crude oil so as to leave only high molecular weight oils in the residuum.

The precipitate of asphaltenes and resins is then extracted with a solvent which is adapted to dissolve the resins and to precipitate the asphaltenes. It is desirable, however, to control extraction conditions and/or solvent to leave the heavier resins with the asphaltenes. For this purpose, I may employ such solvents as petroleum ether or a mixture of butane and iso-pentane or a mixture of naphtha and propane. In the drawings, the asphaltene-resins mixture is extracted with about 3 to 4 volumes of petroleum ether at a temperature of about 175° F. to effect the separation of resins from asphaltenes. The precipitate of asphaltenes containing preferably the heavier resins is next subjected to distillation to remove petroleum ether. The bottoms are then blended in the desired proportion with the resin-free oil previously separated from the residuum. The blend is next subjected to oxidation with air or other oxygen containing gas for a short period of time to oxidize the blend to the desired finished product.

In Fig. 2 of the drawings, the residuum produced as in Fig. 1 is first extracted with the solvent which is adapted to dissolve substantially all of the oil and resins, preferably only the lighter resins and to leave the asphaltenes and preferably the heavier resins as an undissolved precipitate. For this purpose, petroleum ether or a mixture of butane and iso-butane or a mixture of propane and naphtha may be used as described in connection with the process of Fig. 1. The solvent, in this case, petroleum ether, is then stripped from both the solution and the precipitate.

The oil containing the undesirable resins, i. e. the light resins, is then extracted with a solvent adapted to precipitate all of the resins from the oil. This may be accomplished by means of propane or any of the solvents described in connection with the first extraction step of the process of Fig. 1 employing approximately 3 to 6 volumes of propane to one of the oil at a temperature of 100° F. and under a pressure of upwards of 125 lbs. per square inch. The propane is then stripped from the oil and also the resins. The oil may then be blended with the separated asphaltenes in the desired proportion and the blend may be air-blown with air or other oxygen-containing gas to the desired grade as in Fig. 1.

Thus, in the description of the drawings, there are two methods for arriving at substantially the same result. To summarize, in one method the undesirable resins are precipitated along with the asphaltenes and are subsequently removed from the asphaltenes whereas in the other, the undesirable resins are extracted with oil and are subsequently precipitated from the oil. As stated previously, it is desirable to carry out the processes so that the heavier resins remain with the asphaltenes so that when the two fractions are blended in the desired proportion a certain amount of high molecular weight resins remain with the composited asphalt to serve as plasticizers in the blending of the asphaltenes with the oil. These resins are converted into stable asphaltenes when the blend is subjected to air-blowing.

The following is submitted as a specific example of my invention which, however, is not to be considered as limiting but merely as illustrative of the invention.

A Santa Fe Springs crude oil was subjected to vacuum distillation at a temperature of about 675° F. to produce a still bottom having a melting point of 165° F. and a penetration of 6 at 77° F. These bottoms were then extracted at 175° F. with 350 volume percent of a solvent mixture composed of 80% butane and 20% iso-pentane to produce approximately 65.5% by weight of an insoluble asphaltene fraction containing heavy resins having a melting point of 220° F. and a

penetration of one at 77° F. and approximately 34.5% by weight of a soluble oil fraction containing light resins having a gravity of 14.3° A. P. I., a viscosity of 1700 seconds Saybolt Universal at 210° F. and viscosity-gravity constant of 0.875.

The oil fraction containing the light resins was then extracted at 100° F. with propane in a three stage countercurrent system employing 500 volume percent of the propane to produce approximately 17.2% by weight based on the original charge of still bottoms, a propane insoluble fraction having a penetration of 25 at 77° F. and a melting point of 128° F. and approximately 17.3% by weight based on the original charge of still bottoms of a propane soluble oil having a gravity of 19.3° A. P. I., a viscosity of 446 seconds Saybolt Universal at 210° F. and a viscosity gravity constant of 0.845.

Approximately 40% by weight of the above resin free oil was blended with 60% by weight of the asphaltene fraction containing the heavy resins and this blend was air blown or oxidized at a temperature of 450–475° F. for about 2–3 hours to produce an oxidized composited asphalt having a melting point of 221° F., penetrations of 12 at 32° F., 21 at 77° F. and 35 at 115° F., a ductility of 1.4 cm. at 77° F., a flash point of 525° F. Pensky-Martens and a weathering life of 106 cycles.

In order to show that the oxidized asphalt produced by deresining the charging stock resulted in a superior product, a straight Santa Fe Springs residuum was oxidized under the same conditions for a period of 18 hours. The product resulting from this oxidation had a melting point of 220° F., a penetration of 24 at 77° F., a flash point of 490° F. and a weathering life of only 32 cycles in the standard weather-ometer test.

In order to compare the resins in the asphaltene fraction which was precipitated with the butane-iso-pentane solvent mixture with the resins dissolved by this solvent mixture and contained in the soluble oil fraction, 400 grams of the asphaltene fraction was extracted at room temperature (77° F.) with 4 liters of 82° naphtha to form an insoluble precipitate of asphaltenes consisting of 21% by weight and a soluble fraction containing the naphtha soluble resins consisting of 79% by weight of the asphaltene-resin charge. The naphtha soluble resins possessed a melting point of 187° F. and penetrations of zero at 32° F. and one at 77° F. The remaining naphtha insoluble asphaltenes were very brittle having a penetration of zero at 115° F., no melting point being obtained since at 500° F. they were still unmelted and started to decompose.

It will be observed that for determining the melting point, penetration, ductility and flash point, the following methods outlined by the American Society of Testing Materials were used:

Melting point, ball and ring method	D–36–26
Penetration	D–5–25

In determining the weathering life of the asphalt described hereinabove, a standard weather-ometer test was employed. The particular test chosen was the well known test which was developed by Dr. Streiter of the U. S. Bureau of Standards.

The term "viscosity gravity constant" has been defined by Hill and Coates in the Journal of Industrial and Engineering Chemistry, of 1928, vol. 20, page 641. This constant is an indication of the paraffinicity or naphthenicity of an oil, a high value representing a high degree of naphthenicity while a low value indicates a relatively greater paraffinicity.

The above description of my invention is not to be construed as limiting but only as illustrative of the invention as many variations may be made within the scope of the following claims.

I claim:

1. A process for producing asphalts having air-blown characteristics which comprises separating an asphalt residuum into an asphaltene fraction, a resin fraction and an oil fraction and blending said oil fraction with said asphaltene fraction to produce a composited asphalt which is substantially free from resins and subsequently oxidizing said blend.

2. A process for producing asphalts having air-blown characteristics which comprises separating an asphalt residuum into an asphaltene fraction, a relatively light resin fraction and an oil fraction and blending said oil fraction with said asphaltene fraction to produce a composited asphalt which is substantially free from light resins and subsequently oxidizing said blend.

3. A process for producing asphalts having air-blown characteristics which comprises mixing an asphalt residuum with a solvent capable of dissolving oil and light resins but incapable of dissolving asphaltenes, mixing said mixture of light resins and oil with a second solvent capable of precipitating said light resins from said oil to produce an oil fraction which is substantially free from light resins, blending said resin-free oil with said asphaltenes which is substantially free from light resins and subsequently oxidizing said blend.

4. A process for producing asphalts having air-blown characteristics which comprises mixing an asphalt residuum with a solvent capable of dissolving oil and light resins but not substantial quantities of heavy resins and asphaltenes, separating the solution of oil and light resins from said asphaltenes and heavy resins, mixing said oil and light resins with a second solvent capable of precipitating said light resins from said oil, separating a solution of oil and solvent from precipitated light resins, blending said oil with said asphaltenes and heavy resins to produce a composited asphalt which is substantially free from light resins and subsequently oxidizing said blend.

5. A process as in claim 4 in which said first named solvent comprises a mixture of butane and iso-pentane and said second named solvent comprises propane.

6. A process for producing asphalts having air-blown characteristics which comprises mixing an asphalt residuum with a solvent capable of dissolving substantially resin-free oil but not substantial quantities of resins and asphaltenes, separating the solution of oil from asphaltenes and resins, mixing said mixture of asphaltenes and resins with a second solvent capable of dissolving resins from said asphaltenes, separating the solution of resins from undissolved asphaltenes, blending said resin-free oil with said asphaltenes to produce a composited asphalt which is substantially free from resins and oxidizing said blend.

7. A process for producing asphalts having air-blown characteristics which comprises mixing an asphalt residuum with a solvent capable of dissolving substantially resin-free oil but not

substantial quantities of resins and asphaltenes, separating the solution of oil from asphaltenes and resins, mixing said mixture of asphaltenes and resins with a second solvent capable of dissolving light resins but not substantial amounts of heavy resins and asphaltenes, separating the solution of light resins from the undissolved heavy resins and asphaltenes, blending said resin-free oil with said asphaltenes and heavy resins to produce a composited asphalt which is substantially free from light resins and oxidizing said blend.

8. A composited asphalt produced from an asphalt residuum which comprises a blend of asphaltenes and oil, said composited asphalt being substantially free from light resins contained in said asphalt residuum and having air-blown characteristics and weathering life substantially greater than an oxidized asphalt produced by air-blowing said asphalt residuum without prior separation of resins therefrom to a melting point substantially the same as that of said composited asphalt.

9. A composited asphalt produced from an asphalt residuum which comprises a blend of asphaltenes and oil, said composited asphalt being substantially free from light resins contained in said asphalt residuum and having air-blown characteristics and a weathering life substantially greater than an oxidized asphalt produced by air-blowing said asphalt residuum without prior separation of resins therefrom to a melting point substantially the same as that of said composited asphalt, said composited asphalt having a melting point of about 221° F., penetrations of about 12 at 32° F., 21 at 77° F. and 35 at 115° F., a ductility of about 1.4 cm. at 77° F., a flash point of about 525° F. and a weathering life of about 106 cycles.

DONALD E. CARR.