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MANUFACTURE OF ASPHALTS

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10 Claims. (Cl. 196—74)

This invention has to do with asphaltic products of the kind used for paving and similar uses, and with methods of manufacture of such products, and particularly with products of that type having certain requisite properties.

For most convenient definition of the particular field of high grade asphaltic products with which this invention is concerned, as well as to point out what are considered desirable properties of such products, attention is called to the following condensation of the specifications of the city of New York pertinent to two products of the type herein discussed.

CITY OF NEW YORK

ASPHALTIC CEMENT—TENTATIVE 24-A-7A

C Penetration

At 32° F., 100 grams, 5 sec.—Not less than 3
At 77° F., 100 grams, 5 sec.—30–40, 40–50, 50–60 or 60–70 as called for
At 100° F., 100 grams, 5 sec.—Not more than 4 times that at 77° F.

G Ductility

At 77° F., not less than 40 centimeters at 50 penetration

CITY OF NEW YORK

JOINT FILLER—34-A-9

5 Penetration

At 32° F., 100 grams, 5 sec.—Minimum 4
At 77° F., 100 grams, 5 sec.—60–100
At 100° F., 100 grams, 3 sec.—Maximum 3.25 times that at 77° F.

9 Ductility

At 77° F., not less than 40 centimeters

The most pertinent of the properties pointed out above from the standpoint of this invention are penetration and ductility, since it is essential that the asphaltic material to be employed for the purposes contemplated be of proper hardness, as determined by penetration tests, and of major importance, it must simultaneously be of low temperature susceptibility and of high ductility. These important properties (as measured by standard methods of tests of the American Society for Testing Materials) have the following significance. Penetration is a measure of consistency and hardness, serving primarily to classify asphalts into commercial grades of various degrees of hardness. Temperature susceptibility is the ratio of penetrations at various temperatures, for instance, at 100° F. and 77° F. as indicated in each of the above specifications and indicates the susceptibility of the product to change of hardness with change in temperature, that is, its rate of softening. It is desirable that temperature susceptibility as expressed by the above indicated ratio be as low as possible, since if it is too high, those asphalts which have suitable hardness for cold weather will flow and be deformed in warm weather, and, conversely, those suitable for warm weather will be too brittle for cold weather use. Ductility is a measure of the cementing power of the asphalt, that is, of its power to hold together the aggregate or other mineral filler in the final pavement compound. Asphalts having little ductility when used in paving mixtures produce mixtures which separate and disintegrate under conditions of use.

At the present time, asphalt manufacturers are dependent upon the fortuitous presence of desirable properties in selected crude oils for their attainment of the above properties. They may make asphalts only from asphaltic or naphthenic crudes or from asphaltic or naphthenic residues from mixed base crudes. Such crudes, roughly in the order of their desirability, are Mexican, Venezuela, Smackover, California, and Coastal. The best crudes, Mexican, can be steam refined to give asphalts, but for those grades requiring low susceptibility, as typified by the above specifications, they must be oxidized by air blowing. Air blowing always results in loss of ductility, and to get satisfactory ductility on asphalts requiring very low susceptibilities, resort must be made to very careful selection of crudes, even among the best Mexican and Venezuelan stocks, with an almost total inability to produce desired grades from domestic crudes.

A primary object of the present invention is to produce asphaltic compositions combining the properties of high ductility and low temperature susceptibility, which are especially suitable for employment in road surfaces and the like; and it is a further object of the invention to obtain useful materials of the type referred to from crudes, distillates, residua, and other oils which have not heretofore been employed for this purpose and many of which have been waste products. A particular object of this invention is the employment of certain materials which may be processed to asphaltic materials of excellent (low) temperature susceptibility but poor ductility, together with other materials which may be processed to asphaltic products of exceptional ductility and poor (high) temperature suscepti-

bility, to produce finished asphaltic materials of highly desirable qualities.

This invention is based upon the discovery that by solvent refining of distillation products and by distillation alone, numerous stocks of various characteristics are made available, many of which may be used in accordance with the methods herein disclosed to produce asphalts of desirable qualities which heretofore could have been produced only from especially selected Mexican crudes or similar stocks.

In accordance with this invention the field of petroleum distillates and residues, single solvent tars, double solvent tars, and bituminous precipitates may be divided into the following groups of products:

1—Those products capable of being oxidized or otherwise processed to asphaltic products having low (good) susceptibility to change in temperature, but deficient in ductility or entirely without that property.

2—A group of products capable of being oxidized or processed to products of high (poor) susceptibility to change in temperature, and possessed of unusually high ductility.

3—A class consisting of a few members which may be oxidized to products of low susceptibility and acceptable ductility. These occur naturally in the crudes.

4—A group of products entirely without desirable properties of susceptibility or ductility, so highly bituminous in nature that they do not normally admit of processing.

This invention teaches the combination of members of the first and second classes followed by proper treatment, such as blowing, to bring about the production of asphaltic materials having desirable properties as good or better than can be produced from members of the third class, many of the members of the second class being trade wastes and hereby being raised into a field of premium value.

The members of the first class above described are the distillates and residues of paraffinic and mixed base crudes, and single solvent tars and double solvent tars from paraffinic stocks. The members of the second class are the single solvent of double solvent tars or asphaltic stocks derived from asphaltic crudes and mixed base crudes, and pressure still tars. The members of the third class are those few naturally occurring asphaltic residues which may be oxidized or otherwise processed directly to desirable products, such as Mexican and Venezuelan crudes. The fourth class consists of the relatively pure bitumens produced, for example, by treating asphaltic or mixed base crudes with asphalt precipitants, such as propane.

The following short discussion will define, for the purposes of this invention, the terms single solvent tar, double solvent tar and asphaltic or bituminous precipitates. Solvent refining is a process of refining wherein a petroleum product in liquid form is admixed with a solvent liquid which has preferential solvent powers for one of the varieties of compounds therein, for the purpose of separating the oil into two fractions of differing natures. Solvent refining processes may be grouped as follows:

1—Single solvent processes in which only one solvent reagent is used

(A) Naphthenic solvent. Solvents such as phenol, cresol, nitrobenzene, furfural, dichlorodiethylether, liquid sulfur dioxide; etc., which dissolve the naphthenic fraction and remove it as an extract, usually contaminated with some paraffinic material, depending upon the selectivity of the solvent.

(B) Asphaltic precipitants. Liquefied propane, or other light hydrocarbons, alcohols, and the like, which dissolve paraffinic and naphthenic materials and precipitate bitumen from the treated oil. A highly selective process, the bitumen being relatively pure and free from oils.

2—Double solvent processes

Naphthenic solvents and asphalt precipitants, used together, preferably in countercurrent relation. Highly selective operations, in which solvent tar is relatively free from paraffinic materials, but contains naphthenic oil in admixture with asphaltic constituents. (Such processes are exemplified and explained by Tuttle, U. S. Patent Reissue 19,763.)

Where used in the claims, the term "single solvent tar" refers to a tar produced by method 1—A above, and specifically excludes precipitated asphaltic materials produced by method 1—B above. These single solvent tars originate from distillates and residues of highly paraffinic crudes, from distillates of mixed base crudes, and from distillates of asphaltic crudes. Since properties of single solvent tars vary with origin, the mention, in the claim, of the origin of the single solvent tar is also a portion of the definition of that material claimed. Where used in the claims, the term "double solvent tar" refers to a tar produced by method 2 above, and for complete definition of a particular stock requires mention of source of tar in the same manner.

To illustrate the production of asphaltic materials of highly desirable qualities by the combination and proper processing of members of the first two classes above described, there are presented the following examples:

(1) When a paraffinic crude distillate is mixed with a double solvent tar and blown to a proper consistency, the product is one of such desirable characteristics that it might be designated a "Super Mexican Asphalt". Such a product may be made by combining a paraffinic distillate of the type "Red Oil" and a double solvent tar from a mixed base crude, the properties of the ingredients and of the product are as follows:

Properties of double solvent tar from mixed base (Mid-Continent) Crude

Specific gravity at 77/77° F.	1.006
M. P. (R. & B.) °F.	86.5°
Pen. 77° F., 100 grams, 5 sec.	Soft
Pen. 32° F., 200 grams, 60 sec.	91
Pen. 32° F., 100 grams, 5 sec.	19
Vis. Saybolt furol at 210° F.	153''
Flash C. O. C.	510° F.

Properties of solar red oil distillate

Gravity ° A. P. I.	23.0°
Vis., S. U. at 100°F.	315''
Flash, C. O. C., °F.	410°
Pour point, ° F.	20

Properties of blown asphalts produced from blend of 75% of above double solvent tar and 25% of above red oil

M. P. °F.	124.0	128.0	131.0
Pen. 77° F., 100 grams, 5 sec.	66	55	46
Pen. 32° F., 200 grams, 60 sec.	26	23	20
Pen. 32° F., 100 grams, 5 sec.	7	5.5	4.5
Pen. 100° F., 100 grams, 5 sec.	215	172	145
Ductility at 77° F., cm.	100+	100+	100+
Temperature susceptibility (100° F./77° F.)			3.13

For comparison a corresponding asphalt of normally excellent quality produced direct from

good Mexican crude residuum to meet the same specifications is shown below:

MEXICAN ASPHALT

Penetration

32° F., 100 grams, 5 sec.	4
77° F., 100 grams, 5 sec.	55
100° F., 100 grams, 5 sec.	180

Ductility

At 77° F., cm.	100+
Temperature susceptibility (100° F./77° F.)	3.27

It will be noted that the susceptibility of the synthetic product is better than that of the Mexican product, and while both ductilities are above the range of the standard test, inspection by other means shows the synthetic product to be materially better.

(2) Similarly, good products may be made by taking a single solvent tar from a paraffin base overhead distillate, reducing it if necessary by distillation to a viscosity in the neighborhood of 100 seconds Saybolt Universal at 210° F., blending it in equal proportions with the double solvent tar above noted, and air blowing. The resulting product possesses the following excellent properties:

M. P. (B. & R.) °F.	128.0
Pen. 77° F., 100 grams, 5 sec.	53
Pen. 32° F., 200 grams, 60 sec.	25
Pen. 32° F., 100 grams, 5 sec.	7
Pen. 100° F., 100 grams, 5 sec.	170
Ductility at 77° F., cms.	100+
Solubility in CS_2, %	99.93
Flash C. O. C., °F.	440
Temperature susceptibility (100° F./77° F.)	3.21

(3) In this example the double solvent tar above noted was blended with a bright stock produced as a residue from a mixed base crude, and blown, the resulting product having the following desirable properties:

Properties of blown asphalt from blend of 75% of double solvent tar and 25% of bright stock

M. P. °F.	124.5	127.5	132.5
Pen. 77° F., 100 grams, 5 sec.	66	52	42
Pen. 32° F., 200 grams, 60 sec.	24	23	17
Pen. 32° F., 100 grams, 5 sec.	6.0	5.0	3.5
Pen. 100° F., 100 grams, 5 sec.	218	171	129
Ductility at 77° F., cm.	100+	100+	100+
Temperature susceptibility (100° F./77° F.)			3.29

In one of its aspects, this invention discloses the production of desirable asphaltic products combining good (low) temperature susceptibility with high ductility by combining solvent tars produced by the action of single solvents or double solvents upon stocks from asphaltic or mixed base crudes with paraffinic oils (distillates or residues) of relatively high paraffinity followed by blowing the mixture to produce asphalt. The paraffinic distillates or residues which may be used are those which have a viscosity index of not less than 50, and they may be used in varying proportions, depending upon the relative specifications of temperature susceptibility and ductility to be met, with a maximum percentage of paraffin stock in the mixture to be blown of approximately 75%. In these mixtures the paraffin stock contributes the good temperature susceptibility, while the solvent tar contributes the high ductility. For asphalt combining the particular relative specifications of susceptibility and ductility typified by the New York specifications above quoted, a mixture of about 75% solvent tar and 25% paraffinic oil is preferred.

In another aspect this invention discloses the combination of solvent tars produced by single or double solvent treatment of stocks from asphaltic and mixed base crudes with solvent tars produced by single or double solvent treatment of stocks from high paraffinic crudes, followed by processing to produce desirable asphalts combining good temperature susceptibility with high ductility. In these mixtures the solvent tars from highly paraffinic stocks contribute the susceptibility factor, while as before the solvent tars from asphaltic and mixed base crude stock contributes the ductility.

In another aspect this invention teaches the substitution of pressure still tar, that is petroleum residue produced by the cracking of a distillate charge oil, for all or a part of the solvent tars of asphaltic or mixed base stocks in the two procedures outlined above.

It is understood that relatively pure bitumens as separated by solvent refining with asphalt precipitants are not to be confused with solvent tars in the consideration of this invention, because these relatively pure bitumens have very poor (high) temperature susceptibility and low ductility, and are not capable of modification by the methods herein disclosed to asphaltic products of desirable properties combining good (low) temperature susceptibility and high ductility. They are further distinguished from the solvent tars with which this invention is concerned in that while the solvent tars may contain some amounts of these bitumens, the bulk of the solvent tars is made up of resins and of oils of a generally naphthenic character which are not found in appreciable amounts in the materials separated from oils by treatment with asphaltic precipitants, such as propane.

It will be seen that the invention herein disclosed furnishes a method whereby there may be produced materials for the purposes contemplated, combining unusually good and desirable qualities, and that these materials may be so produced entirely from domestic sources, and indeed from many materials which are otherwise waste products, and importation of specially selected crudes of foreign origin may be avoided. It will also be noted that this invention teaches methods whereby these desirable properties may be attained in a degree even beyond the reach of materials of foreign origin heretofore used for the purpose. It teaches methods of processing and selection of stocks in such manner that the relatively strict specifications of certain large users may be met with very considerable degree of ease. Since the method of blowing employed may be any of those commonly used, and effective for the purpose intended, it does not require the installation of equipment of types not already existing.

In summation, it may be stated that in asphalts a ductility of greater than 100 is excellent, or from 100 to 40 is good, and below 40 is poor, when tested at the specified 5 centimeter rate at 77° F., and that in these asphalts temperature susceptibility expressed as a ratio between the penetration at 100°, 100 grams and 5 seconds, and the penetration at 77°, 100 grams and 5 seconds, is excellent when that ratio is less than 4.0, and that this invention teaches methods of processing whereby it is possible to combine excellent ductilities of the order of 100+ with temperature susceptibility ratios ranging from 4.5 downward to about 2.3.

We claim:

1. That method of producing asphalts combining the properties of low (good) temperature susceptibility with high ductility, which comprises the following steps: Mixing a material selected

from the group which consists of single solvent tars of asphaltic and mixed base residual stocks, and double solvent tars of asphaltic and mixed base residual stocks, with a residual petroleum stock, sufficiently paraffinic to have a viscosity index of not less than 50, and blowing the mixture with air until an asphaltic product is produced having a low temperature susceptibility and high ductility.

2. That method of producing an asphalt which comprises the following steps: Mixing a material selected from the group consisting of single solvent tars of asphaltic and mixed base residual stocks and double solvent tars of asphaltic and mixed base residual stocks with a material selected from the group consisting of the heavier oil distillates of paraffinic and mixed base crudes, residues of paraffin base crudes single solvent extracts from paraffinic stocks, and double solvent extracts from paraffinic stocks, and oxidizing the mixture until an asphaltic product is produced having a ductility at 77° F. of at least 100 centimeters, and a ratio of penetration at 77° F. and 100° F. of not greater than 3.5.

3. That method of producing an asphalt which comprises the following steps: Mixing a double solvent tar from residual stock derived from mixed base petroleum with a paraffin oil distillate having a viscosity index of not less than 50, and oxidizing the mixture until an asphaltic product is produced having a ductility at 77° F. of at least 100 centimeters, and a ratio of penetrations at 77° F. and 100° F. of not greater than 3.5.

4. That method of producing an asphalt which comprises the following steps: Mixing a double solvent tar from a residual stock derived from a mixed base crude with a single solvent extract derived from a paraffinic stock, and oxidizing the mixture until an asphalt product is produced having a ductility at 77° F. of at least 100 centimeters, and a ratio of penetrations at 77° F. and 100° F. of not greater than 3.5.

5. That method of producing an asphalt which comprises the following steps: Mixing a solvent tar containing asphaltic matter which, when oxidized to any penetration down to 30, has a ductility at 77° F., not less than 100+ centimeters, with a heavy paraffin oil distillate which, when oxidized to any penetration down to 60, has a ratio of penetrations at 77° F. and 100° F. of not more than 2.0, and oxidizing the mixture until an asphalt product is produced having a ductility at 77° F. of at least 100 centimeters, and a ratio of penetrations at 77° F. and 100° F. of not greater than 3.5.

6. The method of producing asphaltic products with low temperature susceptibility and high ductility which comprises blending a material selected from the group consisting of the heavier oil distillates of paraffinic and mixed base crudes, residues of paraffin base crudes, single solvent extracts produced from paraffinic stocks, and double solvent extracts produced from paraffinic stocks, with a material selected from the group consisting of single solvent tars of asphaltic and mixed base residual stocks and double solvent tars of asphaltic and mixed base residual stock and blowing the blended mixture with air until the mixture has a low temperature susceptibility and high ductility.

7. The method of producing asphalts combining the properties of low temperature susceptibility with high ductility, which comprises the following steps: Blending a material which when oxidized is possessed of low ductility and low temperature susceptibility selected from the group consisting of heavier oil distillates of paraffinic and mixed base crudes, residues of paraffinic base crudes, single solvent extracts produced from paraffinic stocks and double solvent extracts produced from paraffinic stocks, with a material which when oxidized is possessed of high ductility and high temperature susceptibility selected from the group consisting of single solvent tars of asphaltic and mixed base residual stocks and double solvent tars of asphaltic and mixed base residual stocks, and oxidizing the mixture to an asphalt having a low temperature susceptibility and high ductility.

8. The method or producing asphaltic products with low temperature susceptibility and high ductility which comprises blending a material selected from the group consisting of residues and the heavier oil distillates of paraffinic base crudes and solvent extracts of paraffinic base stocks with a material selected from the group consisting of solvent tars of asphaltic and mixed base residual stocks and blowing the blended mixture with an oxidizing gas to produce an asphalt having low temperature susceptibility and high ductility.

9. As a new composition of matter, a blown petroleum asphaltic product possessing relatively high ductility and relatively low temperature susceptibility, produced by admixing a material from the group consisting of solvent tars from asphaltic and mixed base residual stocks with a material from the group consisting of the heavier oil distillates of paraffinic and mixed base crudes, residues of paraffinic base crudes and solvent extracts from paraffinic base stocks and oxidizing said mixture to produce the desired asphaltic product.

10. As a new composition of matter, an oxidized petroleum asphaltic product having a ductility at 77° F. of at least 100 cm. and a ratio of penetrations at 77° F. and 100° F. of not greater than 3.5 produced by admixing a solvent tar containing asphaltic matter which when oxidized to any penetration down to 30 has a ductility at 77° F. not less than 100 cm. with a material from the group consisting of residues of paraffinic base crudes, the heavier oil distillates of paraffinic and mixed base crudes and solvent extracts from paraffinic base crudes and oxidizing said mixture to produce the desired asphaltic product.

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CERTIFICATE OF CORRECTION.

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VLADIMIR L. SHIPP, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 48, for the word "of" read or; same line, for "or" read of; page 4, second column, line 25, claim 8, for "or" read of; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 28th day of February, A.D. 1939.

Henry Van Arsdale.

(Seal)

Acting Commissioner of Patents.