

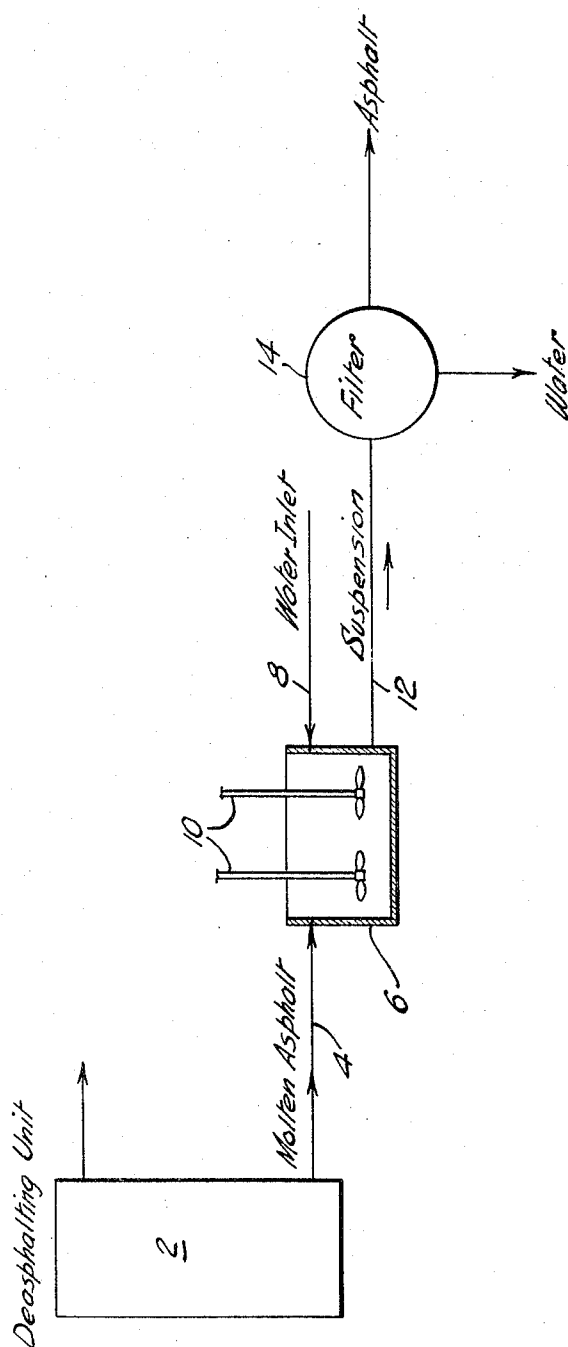
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METHOD OF PREPARING FINELY-DIVIDED ASPHALTIC MATERIAL

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METHOD OF PREPARING FINELY-DIVIDED ASPHALTIC MATERIAL

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This invention relates to a method of preparing powdered asphaltic material, and, more particularly, to a method of preparing finely-divided solid particles of asphaltic material.

Asphalts occur in certain petroleum crude oils, and may be obtained therefrom as a residuum on vacuum distillation or on solvent deasphalting of the crude. The resulting asphalt obtained from the crude may be further treated as by air blowing to improve the plastic and elastic properties of the asphalt. Asphalts are generally regarded as complex systems consisting essentially of highly carbonaceous asphaltenes colloiddally dispersed in a hydrocarbon oily medium, and hydrocarbon resins which act as stabilizers.

In recovering asphalt from crude oil, the crude may be topped to separate the light fractions (gasolines, kerosene and gas oil) leaving a residue comprising the heavier oil fractions and asphalt. The residue from the topping operation is preheated and passed to a fractionating column under high vacuum. The asphaltic residuum is withdrawn at the bottom of the column, and the occluded oil is removed upon steam stripping.

In solvent deasphalting, the residue from the topping step is passed to a liquid-liquid contacting tower near the top in countercurrent contact with propane introduced at the bottom. Propane is a solvent for the asphalt, and as the temperature of the propane is increased, the solubility of the asphalt decreases. The soluble portions of the feed charge pass upward with the propane, and the asphaltic materials pass downwardly and are removed at the bottom. The operating conditions in the tower are closely controlled to effect some refluxing of the oil thereby improving the separation. The asphaltic residuum contains some propane, and the hot mixture is passed to flash drum where the propane is flashed off. Any remaining propane or occluded oil is removed on steam stripping.

Asphalts exhibit definite plastic or flow characteristics the most important of which are penetration and softening point measured in accordance with certain empirical tests as established by the American Society for Testing Materials (ASTM). The penetration (ASTM D5-52) is determined by measuring the distance in tenths of a millimeter that a standard needle penetrates into the asphalt under controlled conditions with a definite load, e.g. 100 grams, and at 77° F. The softening point (ASTM D36-26) is determined by filling a brass ring $\frac{3}{8}$ inch in diameter with asphalt, placing a $\frac{3}{8}$ inch steel ball on the asphalt, and raising the temperature uniformly until the ball drops through. Thus, the consistency for asphalts measured in terms of ASTM penetration at 77° F. with a load of 100 grams may range from 0-3 for a very hard asphalt to about 300 for a very soft asphalt, and the ring and ball softening point for asphalts may range from about 100° F. to 350° F. or higher, the higher softening point generally indicating a harder asphalt.

Furthermore, asphalts vary substantially in rate of change of consistency with change in temperature. This property, which is commonly referred to as susceptibility, depends on the crude source of the residuum from which the asphalt is made, and on processing conditions. A

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number of "susceptibility indexes" have been proposed, among which perhaps the most readily measurable is that of Pfeiffer and Van Doormaal, National Petroleum News 30, R-78 (1938). This index, which correlates the ASTM penetration at 77° F. with the ASTM ring and ball softening point, ranges from a value of -5 for asphalts highly susceptible to change in consistency with change in temperature, to a value of +10 for asphalts of relatively very low susceptibility.

Certain uses require the asphalt to be in a finely-divided state or in particulate form. However, to the best of our knowledge, powdered asphalts have been obtained only with (a) very hard grades of high softening point, i.e. having an ASTM penetration at 77° F. of 5 or less and an ASTM ring and ball softening point of above 250° F., or (b) in the case of lower softening point products (150-200° F.), having a susceptibility index in the range of zero to -5 as determined by the aforementioned procedure. These materials are usually powdered by mechanical attrition.

This invention has therefore as its primary object to provide a method of preparing powdered asphaltic material. It is a more specific object of the invention to provide a method of preparing asphalt in powdered form by employing as a starting material an asphalt characterized by a relatively high penetration, low softening point and low susceptibility and consequently cannot be powdered by conventional mechanical methods.

In accordance with our invention, finely-divided asphaltic material is prepared by initially melting the asphalt. The melted asphalt is contacted under agitation with an anti-coalescing liquid in which the asphalt is relatively insoluble and which is relatively cool in comparison with the melting point of the asphalt being prepared in finely-divided form. Upon agitation, the asphalt separates from the mixture as a finely-divided material which is recovered by filtration, centrifuging, decanting or the like.

Describing our invention in greater detail, the asphalt undergoing treatment is heated to its softening point or higher to render the asphalt sufficiently fluid. If on melting the asphalt, it is heated to too high a temperature, the asphalt may decompose, and therefore a temperature of not more than about 200° F. above the softening point is used, and preferably about 100 to 150° F. above the softening point. The melted asphalt is contacted under agitation with an anti-coalescing liquid, for example water, in which the asphalt is relatively insoluble. Thus, for example, the water may be agitated as the asphalt is added to the water. The water as the anti-coalescing liquid is maintained at a relatively cool temperature, usually not less than 75° F. cooler than the softening point of the final asphaltic product to be prepared in powdered form, and more preferably not less than 100° F. It is advantageous to employ an excess of water in order that the molten asphalt may be completely immersed in the aqueous mixture. Agitation as used herein and in the appended claims, is defined as violent and irregular movement whereby intimate contact between the asphalt and water occurs and discrete particles of the asphalt undergoing treatment separate. If the asphalt upon contact or mixing is not agitated, or if only mildly stirred, the material undergoing treatment will agglomerate. Agitation may be satisfactorily accomplished by high speed stirring, as for example with paddle stirrers or impeller stirrers rotating at high speeds, or with a turbine mixer, mixing valve, centrifugal pump, orifice nozzle, etc. This treatment dissociates the asphaltic material into discrete particles which separate from the remaining aqueous phase in finely-divided form. A film of liquid used in the dissociating step coats or surrounds the asphaltic particles which prevents the particles from coalescing. For this

reason, we have employed herein the term "anti-coalescing liquid." The fine particles of asphalt may be separated from the remaining aqueous mixture by filtration and dried by conventional means at relatively low temperatures and in air, if desired, to recover the asphalt in powdered form.

It should be understood that although the invention has been described in more detail in connection with the use of water as the particular anti-coalescing liquid, other liquids are satisfactory and may be employed in the process. Thus, aqueous mixtures of glycol and glycerol and of alkanols and ketones having 1 to 4 carbon atoms, for example, methanol, ethanol, propanol, isopropanol, etc. and acetone and methyl ethyl ketone may be advantageously employed. Such mixtures preferably contain about 25% to 60% by volume of the organic liquid, the balance being water.

Where desired, a minor amount of a suitable surface active agent such as the sodium sulfonates may be incorporated in the anti-coalescing liquid. The surface active agent facilitates separation of the finely-divided asphaltic material from the aqueous mixture, and reduces the quantity of water entrained by the recovered powdered product. The choice of surface active agent is determined largely by the materials employed in the process, and may be anionic, cationic or nonionic. About 0.1 to 0.5 percent by weight of surface active agent may be incorporated by dissolving the agent in the anti-coalescing liquid, but smaller or larger amounts may be used where desired.

In addition, a small amount of a hydrophobic micro-dimensional silica powder may be incorporated in the powdered product. The amount of silica powder used depends somewhat upon the consistency or hardness of the asphalt being treated, in that the harder grades would require somewhat smaller amounts of silica powder, but generally about 0.5 to 5 percent by weight is satisfactory. The silica powder facilitates the separation of the finely-divided asphaltic material from the aqueous mixture, and further assists in maintaining the powdered asphalt in a dry condition and therefore free flowing.

Where deemed desirable, finely powdered calcium silicate, which may be synthetically prepared, may be admixed with the powdered asphaltic product to maintain it in a free flowing condition. The calcium silicate should have a surface area of from about 95 to 200 square meters per gram and an ultimate particle size of 0.1 micron. Here again, the amount of calcium silicate used depends somewhat upon the consistency of the asphalt being treated, but generally about 1 to 15% by weight is satisfactory. The calcium silicate may be admixed with the powdered asphaltic material immediately upon recovery from the solution as by filtration, and the resulting admixture dried at a temperature of from about room temperature to 115° F. Other finely powdered materials which may be employed as an alternative to the calcium silicate include talc, diatomaceous earth, and bentonite.

It will be observed that the asphaltic residuum obtained upon deasphalting of crude oil by vacuum fractionation or by propane deasphalting may be rendered directly in powdered form. This may be more clearly illustrated by reference to the accompanying drawing. Numeral 2 represents a deasphalting operation which we may assume is operated under conditions that result in a normally solid asphalt product upon cooling. For purposes of the illustration, the deasphalting operation may include steam stripping to remove occluded oil, flashing to remove the propane used in solvent deasphalting, and other preliminary treatments. The asphalt, while in molten condition, is passed from the deasphalting operation via line 4 to a vessel or tank 6 of any desired capacity. Water is contained in vessel 6 and may be added thereto via line 8 from a source not shown. The asphalt is contacted with the water under agitation provided by impeller stirrers 10 whereby the asphalt separates as a

finely-divided material as explained above. The resulting powdered asphaltic product is in aqueous suspension or slurry and is withdrawn from the bottom of the vessel via line 12 which is oppositely disposed to inlet line 4. The suspension is passed to a filtration unit 14 where the powdered asphalt is separated from the water. When deemed desirable, the flow of asphalt and water to vessel 6 may be interrupted and the powdered asphalt separated from the water. In this manner, filtration unit 14 is eliminated from the over-all operation. When deemed desirable, a surface active agent may be added to vessel 6. In addition, one of the fine powders to maintain the asphalt product dry and free flowing such as silica powder or calcium silicate (as explained above) may be added to vessel 6, or may be admixed with the asphalt recovered from filter 14.

Conducting the process of our invention in combination with the deasphalting operation is particularly advantageous in that the asphalt is molten and may be immediately rendered powdered. The powdered product not only has several uses, but, equally important, as a powder, transportation of the asphalt is greatly facilitated.

As illustrative of the process of the present invention, the following examples are given:

Example I

Asphalt having a ring and ball softening point of 265° F. (ASTM D36-26), penetration at 77° F. (ASTM D5-52) of 1 and a susceptibility index of +2.5 was heated to 420° F. About 50 grams of the resulting molten asphalt were poured in a thin stream into about 400 milliliters of water at 60° F. while vigorously stirring in the Waring Blendor operating at 10,000 r.p.m. The resulting mixture was filtered on a Büchner funnel and dried by pulling air through the filter cake. About 50 grams of powdered asphalt was recovered which was free-flowing at room temperature and had a particle size equivalent to about 40 mesh (U.S. Standard Sieve Series).

Example II

Asphalt having an ASTM ring and ball softening point of 190° F., an ASTM penetration at 77° F. of 27 and a susceptibility index of +3.9 was heated to 350° F. About 50 grams of the molten asphalt were added to the cold water as in Example I, and the powdered asphalt recovered upon filtration was air-dried for about 1 hour. The powdered asphalt was intimately admixed with about 3 percent by weight of Estersil, a hydrophobic finely powdered silica manufactured by E. I. du Pont de Nemours and Co., Inc. A gray powdered asphalt was obtained which was found to be free-flowing after 72 hours at ambient temperature.

Example III

28 grams of an asphalt having an ASTM penetration at 77° F. of 39, an ASTM ring and ball softening point of 171° F. and a susceptibility index of +3.3 were heated to 280° F. and poured slowly into 300 ml. water at 60° F. while vigorously stirring in the Waring Blendor. The resulting mixture was filtered on a Büchner funnel, and after substantially all the water adhering to the asphalt had been removed by suction, the asphalt was admixed with 6 grams of Micro-Cel, a calcium silicate manufactured by Johns-Manville. The resulting powdered mixture was allowed to stand overnight in an oven maintained at 110° F. The powdered mixture was then shaken on a 200 mesh screen to remove an excess of Micro-Cel. 3 grams of Micro-Cel were recovered. The recovered asphalt product was a gray, free-flowing granular powder.

Example IV

13.5 grams of an asphalt having an ASTM penetration at 77° F. of 49, an ASTM ring and ball softening point of 155° F. and a susceptibility index of +2.5 were heated to 260° F. and poured slowly into 400 milliliters of water

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at 40° F. while vigorously stirring in the Waring Blendor. The mixture was filtered, and 2.6 grams of Micro-Cel was thoroughly admixed with the resulting filtrate. The admixture was oven dried as in Example III, and then shaken on a 200 mesh screen whereby 2 grams of excess Micro-Cel was recovered. The asphaltic product was granular and free-flowing.

Example V

26 grams of asphalt having an ASTM penetration at 77° F. of 7, an ASTM ring and ball softening point of 205° F. and a susceptibility index of +2.0 were heated to 350° F. 2.5 grams of finely powdered talc were added to 300 milliliters of water at 58° F. The molten asphalt was added slowly to the water while stirring vigorously in the Waring Blendor. The resulting mixture was filtered on a Büchner funnel, the filtrate air dried for 2 hours and further dried in a vacuum desiccator for 16 hours. An additional 2.5 grams of talc was admixed with the asphaltic material thereby resulting in a free-flowing powdered product.

It will be observed that the asphalts employed in Examples II through V, inclusive, are relatively soft and consequently could not be prepared in finely divided powdered form by the conventional grinding technique.

We claim:

1. A method for preparing an asphaltic powder from asphaltic residuum, said residuum being a solid at room temperature, consisting essentially of heating said asphaltic residuum to a temperature between about 100 and 200° F. above the softening point of said residuum, introducing the resultant molten asphaltic residuum into a pool of an anti-coalescing liquid maintained at a temperature at least 75° F. below that of said softening point while agitating said liquid sufficiently to cause a violent and irregular movement thereof, said anti-coalescing liquid selected from the group consisting of water and 25 to 60 vol. percent aqueous glycol, aqueous glycerol, aqueous alkanol and aqueous alkanone of 1 to 4 carbons, and said anti-coalescing liquid being present in volumetric excess in respect to said residuum, whereby said asphaltic

powder separates from the final liquid phase and recovering said powder.

2. A method in accordance with claim 1 wherein said anti-coalescing liquid is water.

3. A method for preparing an asphaltic powder from asphaltic residuum, consisting essentially of heating said asphaltic residuum to a temperature between about 100 and 200° F. above the softening point of said residuum introducing the resultant molten asphaltic residuum into a pool of a volumetric excess of an anti-coalescing liquid maintained at a temperature at least 75° F. below that of said softening point while agitating said liquid sufficiently to cause a violent and irregular movement thereof, whereby said asphaltic residuum separates as a powder, recovering said powder from said resultant liquid and contacting said powder with a hydrophobic anti-caking agent, said anti-coalescing liquid selected from the group consisting of water and 25 to 60 vol. percent aqueous glycol, aqueous glycerol, aqueous alkanol and aqueous alkanones of 1 to 4 carbons, and said anti-caking agent selected from the group consisting of silica, calcium silicate, talc, diatomaceous earth and bentonite.

4. A method in accordance with claim 3, wherein said anti-coalescing liquid is water and said anti-caking agent is calcium silicate.

5. A method in accordance with claim 3, wherein said anti-coalescing liquid is water, said anti-caking agent is talc.

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