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METHOD FOR PRODUCING ASPHALT

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This invention relates to an improved coating or air-blown asphalt and to a process for manufacturing the same.

It is well recognized in the art of manufacturing air-blown i. e. oxidized or coating type 5 asphalts, that these products may be prepared by blowing the charging stock, such as asphalt residua produced from asphalt-containing crude oils, with air or other oxygen-containing gases at an elevated temperature. The product resulting from this operation will possess desirable low temperature susceptibilities, a higher melting point for a given penetration as compared with unoxidized asphalts and a moderately high ductility. This type of asphalt is generally preferred in the roofing industry.

In recent years, attention has been focused on the light-promoted oxidation of asphalt and as a result of many roof failures, the Minnesota Mining and Manufacturing Company has investigated the effect of light and moisture on asphalt and has devised what is now known as the photosensitivity test. They found that under certain degrees of exposure to light, all asphalts form a thin surface coating of oxidized materials, and that by immersing the exposed asphalt in warm water, the degree of oxidation can be strikingly shown by a color change. Sufficiently oxidized surfaces take on a yellow, paint-like appearance, which has been termed "rust." The length of exposure necessary to develop this rust is taken as an indication of the degree of photosensitivity of the asphalt.

The work of the above Minnesota company was mainly concerned with the loss of adhesiveness of the asphalt for roofing granules in the case of roll roofing or asphalt shingles in which the surfaces are coated with mineral granules which may transmit a certain amount of light. Surface oxidation of the asphalt in the presence of light was assumed by them to correspond to a loss of binding power for the granules. Asphalts which thus show a high degree of photosensitivity according to the photosensitivity test are regarded as unsuitable for use with their granules.

However, an aspect of more serious consequence to the roofing trade in general is the fact that in the light reaction certain acidic water-soluble substances are formed which, if not washed completely off by rain, tend to concentrate in dew puddles and leave yellow stains, especially in hot, moist climates. This is a frequent source of complaint in the case of mopped roofs or built-up roofing. It should be noted that this form of stain, which may also effect the color of granules in shingle-coated roofs, has

nothing whatever to do with the staining due to oil exudation and in fact, is most frequently encountered with certain asphalts which show low stain numbers by the Barber test, which measures the tendency of an asphalt to exude oil.

The fact that the water-soluble portion of these oxidation products is acidic often results in rather extensive corrosion of down spouts, galvanized roof gutters, etc.

Also, it will be noted that the photosensitivity phenomenon has no necessary connection with the fundamental weathering behavior of the asphalt. In fact, some of the asphalts which have the longest Weather-Ometer life are the most photosensitive and conversely, some of the poorest asphalts from a Weather-Ometer standpoint are the best from a photosensitivity standpoint, i. e. are the least photosensitive. Thus, some asphalts which are otherwise considered to be good asphalts and have a long Weather-Ometer life have the disadvantage of being very photosensitive. By Weather-Ometer life is meant the life of an asphalt as measured by the test developed by Dr. Strieter of the U. S. Bureau of Standards.

Thus, it is an object of our invention to produce non-photosensitive asphalts from photosensitive asphalts.

We have found that one of the properties of an asphalt most influencing the photosensitivity test, i. e. resulting in a high photosensitivity, is the presence of a relatively light oil in the asphalt. Our experimentation relating to fractionation of the photosensitive asphalts has shown that the reactive constituents in photosensitive asphalts are confined to the oils and are concentrated chiefly in the relatively light and medium lubricating oils. By vacuum topping, it has been found possible to prepare heavy oils from such photosensitive crude oils as Santa Maria Valley (California) crude oil which are relatively inert to light. Thus, by a suitable fractionation procedure, it is possible to produce from such photosensitive asphalts, a flux, which, upon air blowing to the desired characteristics, is considerably improved in respect to photosensitivity.

We have also found it possible to produce a flux from a photosensitive asphalt, which, upon oxidation with air, results in the production of a relatively non-photosensitive coating asphalt by subjecting the asphalt or topped asphaltic residuum to extraction with solvents which are capable of precipitating the asphaltenes and also resins contained in the asphalt and dissolving the oil fractions therein. We have found that the solvent precipitated asphaltenes and resins are

relatively inert with respect to light. By subjecting the light sensitive solvent soluble fraction to distillation to remove light oils, we have found that the residue consisting of a heavy oil is relatively stable to light, this stability toward light increasing with the boiling range of the heaviest overhead cut removed. By blending the heavy oil bottoms with the precipitated asphaltenes and resins in the desired proportions, a composited asphalt which is stable towards light may be produced and which, if desired, may be air-blown to produce an oxidized asphalt which is stable towards light.

The precipitation of the asphaltenes and also resins may be accomplished by extracting the oil with solvents such as the liquefied normally gaseous hydrocarbons, such as ethane, propane, butane and isobutane or mixtures thereof. The separation with these solvents may be effected by simply mixing the asphalt with the solvent at normal temperatures or more elevated temperature of about 100° F. under pressure sufficient to maintain the solvent in the liquid state at the temperature employed. For example, in the case of propane, approximately three to six volumes of propane may be mixed with the asphalt residuum at a temperature of about 100° F. and a pressure of about 175 pounds per square inch. This mixture is allowed to remain in a quiescent state until the precipitated asphaltenes and resins have settled to the bottom of the container in which the admixture was effected. The clear supernatant solution of oil and propane substantially free from or containing relatively small amounts of resins is decanted from the settled asphaltenes and resins and is subjected to distillation to remove the propane which may be recovered by compression and cooling and returned for further treatment of residuum.

The propane-free oil may then be subjected to distillation and fractionation in order to separate the light oils contained therein which carry the photosensitive materials. The bottoms are then blended in the desired proportion with the previously precipitated asphaltenes and resins, after removal of propane therefrom, to produce a composited asphalt flux which may be oxidized at an elevated temperature with air or other oxygen-containing gas to produce a coating asphalt which is relatively inert to light.

In the foregoing, it may be desirable to remove resins as well as the light oils from the asphalt. It has been found that the presence of resins, particularly the resins of low molecular weight, in the blowing stock are generally responsible for the production of air-blown asphalts which have a relatively low Weather-Ometer life. These resins may be removed by subjecting the propane precipitated asphaltene-resin mixture to extraction with a solvent capable of dissolving the resins, at least the resins of low molecular weight, but not substantial amounts of the asphaltenes at the temperature employed. For this purpose, relatively heavier solvents may be used such as petroleum ether. As an example, three or four volumes of petroleum ether may be mixed with the propane precipitated asphaltene-resin mixture at a temperature of about 175° F. and the mixture allowed to settle. The solution of petroleum ether and resins is next decanted from the settled asphaltenes. The latter is then subjected to distillation to remove any petroleum ether contained therein. The asphaltenes may then be blended with the bottoms resulting from the distillation of the previously propane ex-

tracted oil in such proportions as to produce a flux which may be air-blown to the desired melting point-penetration characteristics.

Experimentation has also shown that materials is asphalt which are responsible for high light sensitivity are aromatic or unsaturated in nature since they may be removed by extraction of the light or medium lubricating oils with a selective solvent capable of separating the oil into a relatively paraffinic fraction and a relatively non-paraffinic or aromatic or naphthenic oil fraction. In order to produce the relatively non-photosensitive asphalt, the asphalt or topped asphaltic crude oil may be subjected to vacuum distillation in order to distill the oil fractions from the asphaltenes or the oils may be separated from the asphaltenes by the aforementioned precipitation with solvents such as propane. The oil is then extracted by known extraction methods with a selective solvent, such as phenol, liquid sulfur dioxide, furfural and the like, to separate the oil into a raffinate phase and an extract phase. The raffinate phase is next stripped of solvent and the raffinate thus produced is blended with the aforementioned distillation bottoms, i. e. asphaltenes, or solvent precipitated asphaltenes in such desired proportions as to produce a composited asphalt which may be used as composited or which may be subjected to mild or more severe oxidation with air or other oxygen-containing gas. If desired, the raffinate oil may be subjected to distillation to remove light oils before being composited with the asphaltenes. These light oils, however, are generally not sensitive to light since the light sensitive materials have been removed by the extraction process and remain in the extract phase.

In order to still further decrease the photosensitivity of the above produced asphalts, small amounts, i. e. 0.5 to 10% by weight of certain inhibitors of photo-oxidation may be mixed with the asphalt. For this purpose, we have found a large number of substances which may be added to the asphalt to reduce photo-oxidation. Compounds that are characterized by polar character, i. e. long hydrocarbon chains terminating in a polar group such as oxygenated groups, nitro groups, sulphenic groups, halogen or aromatic nuclei, have been found to be particularly suitable as inhibitors of photo-oxidation. The higher straight chain fatty acids such as lauric, tridecoic, myristic, pentadecic, palmitic, margaric, stearic, nondecoic, arachidic, eicosic or eicosanic, behenic, tricosic, lignoceric or carnaubic, pentacosic, cerotic, hexacosic, carboceric, montanic acids, and also the alcohols derived from the above higher straight chain fatty acids such as lauryl, oleyl, stearyl, etc., alcohols have been found to be particularly active inhibitors of photo-oxidation. Also, the higher straight chain olefinic acids, undecylinic, myristolenic, palmitolenic, oleic, petroselinic, erucic, brassidic, nervonic and like olefinic acids may be used as inhibitors of photo-oxidation. Likewise, the alcohols derived from these olefinic acids are good inhibitors of photo-oxidation. Montan wax, carnauba wax, hydrogenated fish oil acids, acidulated cocoanut oil acids, acidulated shortening oil acids, cottonseed oil acids, etc., may also be used. Paraffin wax which has been oxidized at relatively low temperatures under conditions favoring fatty acid rather than estolide or hydroxy acid formation has also been found to be an effective inhibitor.

The following are submitted as specific ex-

amples of our invention. These, however, are not to be considered as limiting but merely as illustrative of the invention.

Example 1

A Santa Maria Valley crude oil was topped with steam to produce an asphalt residue having a viscosity of 120 seconds furol at 210° F. This residue was then mixed with four volumes of propane at a temperature of 100° F. under a pressure of 175 lbs. per square inch. The mixture was allowed to remain in a quiescent state at this temperature and pressure in order to permit the precipitated asphalt to settle below the solution of oil and propane. The latter was decanted from the settled asphalt and the two separated fractions were distilled to remove propane therefrom. Approximately 53% by weight of propane soluble oil was obtained having a viscosity of 80 seconds Saybolt Universal at 210° F. and low flash point of 250° F. (Cleveland Open Cup). A portion of this oil was then distilled under vacuum to remove 40% as overhead consisting of light and medium lubricating oils. The bottoms representing 60% of the extracted oil had a viscosity of 450 seconds Saybolt Universal at 210° F.

These bottoms were then blended with a vacuum distilled asphalt produced from the same Santa Maria Valley crude oil having a melting point of 125° F. and a penetration of 40 at 77° F. The blend was effected in the proportions of 60% by weight of the asphalt and 40% by weight of the above bottoms. The composited blend had a viscosity of 378 seconds furol at 210° F. and a flash point of 530° F. (Cleveland Open Cup).

The blend of asphalt and oil was then oxidized with air at a temperature of 400-450° F. for 25 hours, using 5 cubic feet of air per barrel of charge per minute. The oxidized charge showed a melting point of 217° F., penetrations of 14 at 32° F., 18 at 77° F. and 33 at 115° F., a ductility of 4.0 at 77° F., a flash point of 520° F. (Cleveland Open Cup) and a Barber stain number of 2.0.

An aluminum panel was coated with this asphalt to a thickness of 0.025 inch and the coated panel was then exposed to the radiation of a 1500 watt lamp at a distance of 6 inches from the lamp. The panel was exposed for 23 hours and was then immersed in warm water at 140° F. resulting in the formation of a light rust which remained upon drying the panel. No rust was formed on similar panels exposed less than 28 hours.

In order to compare the photosensitivity of the above asphalt with a similar asphalt of 217° F. melting point but which had not been subjected to the process of the above invention, another portion of topped Santa Maria Valley crude oil having a viscosity of 120 seconds furol at 210° F. was oxidized with air to produce an asphalt of 217° F. melting point. An aluminum panel coated as above with this asphalt and subjected to the above photosensitivity test showed a light rust on the surface of the asphalt at the end of eight hours' exposure to the lamp and a heavy rust at the end of twelve hours' exposure.

Example 2

Another portion of the propane extracted oil bottoms having a viscosity of 450 seconds Saybolt Universal at 210° F. of the above example was blended with the propane precipitated asphalt of the above example in the proportions of 40% by weight of the precipitated asphalt and 60%

by weight of the oil bottoms. The blend showed a viscosity of 500 seconds furol at 210° F. and a flash point of 560° (Cleveland Open Cup).

This blend was oxidized with air as previously described to produce an air-blown asphalt having a melting point of 220° F., penetrations of 15 at 32° F., 19 at 77° F. and 31 at 115° F., a ductility of 4.2 and a flash point of 530° F. (Cleveland Open Cup). When a panel coated with this asphalt was subjected to the above photosensitivity test, there was no evidence of rust formation at the end of thirty-two hours' exposure to the lamp.

Example 3

The remaining portion of the propane extracted oil of Example 1 having a viscosity of 80 seconds Saybolt Universal at 210° F. and a flash point of 250° F. was extracted five times at 100° F. with a mixture consisting of 90% phenol and 10% water, using two volumes of selective solvent to one of the oil on each extraction. The raffinate produced by the five extractions had a viscosity of 172 seconds Saybolt Universal at 210° F. and a viscosity gravity constant of 0.836.

The precipitated asphalt of Example 1 which contained resins was extracted with 350 volume percent of petroleum ether at a temperature of about 175° F. to effect solution of the resins in the petroleum ether. The mixture was allowed to settle and the supernatant solution of resins and petroleum ether was decanted away from the settled asphaltenes. The latter was then stripped of the petroleum ether and was blended with the previously described raffinate in the proportions of 60% by weight of the raffinate to 40% by weight of the asphaltenes to produce a blended asphalt having a melting point of 220° F. and a penetration of 40 at 77° F. This blend was then tested, as above, for photosensitivity and showed no rust formation at the end of thirty-two hours.

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

45 Melting point (ball and ring method) -- D-36-26
Penetration ----- D-5-25

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 oil, a high value representing a high degree of naphthenicity, while a low value indicates a relatively greater paraffinicity.

The foregoing description of our 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.

60 We claim:

1. A method for producing relatively non-photosensitive asphalt from relatively photosensitive asphalt which comprises mixing said asphalt with a solvent capable of dissolving oil but incapable of dissolving asphaltenes at the temperature employed, separating a solution of oil in said solvent from said asphaltenes, subjecting said separated oil to extraction with a solvent capable of dissolving relatively non-paraffinic oil fractions but not relatively paraffinic oil fractions, separating said relatively non-paraffinic oil fractions from said relatively paraffinic fractions, distilling said relatively paraffinic fractions to remove light and medium lubricating oils and commingling the remaining heavier paraffinic oil fractions with said

separated asphaltenes to produce a relatively non-photosensitive asphalt.

2. A method according to claim 1 in which said solvent capable of dissolving oil but incapable of dissolving asphaltenes at the temperature employed comprises a liquefied normally gaseous hydrocarbon.

3. A method according to claim 1 in which said solvent capable of dissolving oil but incapable of dissolving asphaltenes at the temperature employed comprises propane.

4. A method according to claim 1 in which said solvent capable of dissolving relatively non-paraffinic oil fractions but not relatively paraffinic oil fractions comprises phenol.

5. A method according to claim 1 in which

said solvent capable of dissolving oil but incapable of dissolving asphaltenes at the temperature employed comprises a liquefied normally gaseous hydrocarbon and in which said solvent capable of dissolving relatively non-paraffinic oil fractions but not relatively paraffinic oil fractions comprises phenol.

6. A method according to claim 1 in which said solvent capable of dissolving oil but incapable of dissolving asphaltenes at the temperature employed comprises propane and in which said solvent capable of dissolving relatively non-paraffinic oil fractions but not relatively paraffinic oil fractions comprises phenol.

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