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BITUMINOUS CEMENT

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The present invention relates to a bituminous cement. The invention relates particularly to bituminous cements or cut-back asphalts intended to be used with earth, sand, gravel and other road building materials for the production of a hardened course but may also be used for other purposes such as penetrating and preserving wood, waterproofing concrete, building or repairing roofs, painting metal, and any of the common uses to which a bituminous paint is ordinarily applied.

The value of bitumen or asphalt as a cementing and protecting agent is well known but it is desired to point out that in order to utilize asphalt for a wide variety of purposes and under various conditions, it has been common practice to cut back or to dissolve the bitumen in a volatile solvent which reduces the viscosity of the bitumen sufficiently to permit efficient application of the bitumen to the problem at hand. Asphalts or bitumens which have been dissolved in a volatile solvent are generally known as "cut-back" asphalts.

When the bitumen is dissolved in a volatile solvent, it may be applied in a cold condition. In recent years, bitumens have been emulsified with water sometimes after partially cutting back to permit cold application. Unless the bitumen is emulsified or cut back, it must be applied hot, that is, in a melted condition and this is often inconvenient or totally impracticable. Directing attention particularly to road building cut-back asphalt consisting of a relatively hard asphalt, say having 50 to 200 penetration at 77° F. and 10 to 50 percent by volume of volatile solvent, is used, for example, as a bituminous cement by admixing with the road building material, i. e. crushed rock, gravel and sand, and then agitating or mixing with the road building material until the bituminous cement is thoroughly incorporated. The finished asphaltic mixture is then spread on the road to secure compaction and consolidation. As the volatile solvent evaporates, the road hardens or takes a "set" as it is commonly called. A common method in laying of low cost roads is to mix the bituminous cement and the road building materials in place upon the road by first spraying the bituminous cement on top of windrowed earth or gravel and then blade mixing back and forth across the road until complete mixing has been obtained. Sometimes mere spraying of the road with oil or cut-back asphalt is used, in which case the treatment is called "penetration" treatment.

The use of road oils, which are generally reduced petroleum residua, is quite similar to the use of cut-back asphalts and probably antedates the use of cut-back asphalts, particularly in the western part of the United States. Both the cut-back asphalts as commonly produced and the residual road oils, may be considered as being a mixture of a hard bituminous component and a less viscous solvent. In the case of the volatile cut-back asphalts, the diluent is a relatively low boiling distillate, whereas in the case of the residual road oils, the diluent consists of naturally occurring heavy gas oil and lubricating oil fractions. Obviously, the road oils are very markedly slower in obtaining their set and it is an open question as to whether an ordinary residual road oil ever reaches a hardened condition corresponding to the true asphalt content.

It is an object of my invention to produce bituminous cements or cut-back asphalts suitable for the above mentioned purposes having remarkable cementitiousness and rapid penetration characteristics and which may be produced at a low cost.

It is a particular object of my invention to produce cut-back asphalts in which a low boiling solvent is formed in situ and which is distinguished from ordinary cut-back asphalts produced by blending a volatile solvent to ordinary asphalts which are hard at ordinary atmospheric conditions of temperature and pressure.

Briefly stated, my invention comprises a process for producing a bituminous cement or cut-back asphalt in which a viscous stock or asphaltic residual oil having a relatively high degree of cementitiousness is cracked to reduce its viscosity and form volatile fractions therein which volatilize subsequent to the application of the bituminous cement. The invention includes a bituminous cement which has been prepared by cracking a viscous asphaltic stock or an asphalt such as a steam refined asphalt to produce fractions in the bituminous cement which will reduce its viscosity and which will evaporate from the bituminous cement upon its application to a road or other places and thus permitting the remainder of the cement to set up or harden.

More specifically stated, my invention resides in a process for producing bituminous cements which are particularly adapted to penetrate into the aggregate of a road or to be mixed therewith and then set up as a hard bituminous cement which comprises subjecting an asphaltic residual oil or topped crude to distillation to produce an asphalt having a relatively high percentage of bituminous material but which is relatively free from fractions which permit is to flow at atmospheric conditions of temperature and pressure, then subjecting the asphalt to restricted conditions of cracking so as to merely reduce the viscosity of the asphalt and permit it to flow freely at atmospheric conditions and containing fractions which will volatilize when applied to the road or other places of use and thus permit the remaining material to set up as a hard bituminous cement.

To produce the cut-back asphalt forming the subject of my invention, I first produce a heavy road oil or paving asphalt, i. e. one substantially free from volatile oils, by any of the conventional methods now known such as by reducing an asphaltic crude oil by fire and steam under vacuum until a heavy road oil or asphalt remains as a distillation bottom which is substantially free from fractions boiling below 700 to 750° F. and containing approximately 80 to 85% of 80 penetration asphalt. I then subject this asphaltic material to high temperatures for a sufficient time to produce by cracking low boiling products which will serve as diluents for the asphaltic component and thus giving a product having viscosity and distillation characteristics analogous to cut-back asphalts produced by adding a volatile diluent to ordinary asphalt. The bituminous cement will contain from 70 to 80% of 80 penetration asphalt and the remainder comprising cracked diluents and oils. In other words, I employ a heavy bituminous material which has a fairly high cementing value but which is so viscous that it cannot be used in an unaltered state except under restricted conditions where heat can be employed. I then subject this asphaltic material to cracking conditions for the purpose of reducing its viscosity and giving a product still having a high asphalt content and which hardens upon exposure in thin films to the atmosphere due to the evaporation of the volatile cracked solvent.

The conditions to be maintained during cracking of the heavy road oil should be well known to those skilled in the art of cracking. The cracking may be carried out in any of the conventional cracking units such as the Cross and Dubbs cracking units. Generally, I prefer to subject the stock to such cracking conditions as will produce up to approximately 40% of volatile oils boiling below 680° F. which are retained in the bituminous content of the stock after cooling the cracked product. The cracking conditions will vary but generally pressures of 400 to 1000 lbs. per square inch and high temperatures of 800 to 900° F. will suffice to give the proper degree of cracking and viscosity reduction. The distillation of volatile solvents produced in the cracking operation is effected only to such extent as will leave a residue of the proper volatility and consistency corresponding to the use to which the bituminous cement is to be applied. If desired, all of the light volatiles except possibly the light fixed gases which are produced in the cracking may be retained in the bituminous cement. However, I prefer to distill off some of the light fractions so as to leave a residue having an initial distillation point of approximately 350 to 450° F. in the liquid. Such a material will correspond to an asphalt which has been cut back with kerosene or heavy gasoline.

In order to retain the volatile cutting solvents in the cracked product or residue, the distillation of the cracked product is carried out under pressure so that only the most volatile fractions are removed by distillation. The object in removing the very light fractions, that is, fractions boiling up to 250° F. by the distillation is to raise the flash point so as to reduce the danger from inflammability during shipping and handling of the bituminous cement. Also, it is desirable in a bituminous cement having a definite viscosity and which is to be used for the purposes described herein that low boiling fractions be absent for the reason that they evaporate too quickly after application of the cement causing an increase in viscosity before the cement has had time to penetrate and coat the particles of the road building materials.

The following is a specific example of a method for carrying out my invention to produce cut-back asphalt. However, it is to be understood that this example is merely illustrative of one embodiment of the invention and is not to be construed as limiting my invention:

A heavy road oil stock produced by topping with fire and steam under vacuum Poso Creek crude oil and having a gravity of 10.4° A. P. I., a flash point of 480° F., a Saybolt furol viscosity of 3000 seconds at 122° F. and 102 seconds at 210° F. and containing about 82% of 80 penetration asphalt and substantially free from fractions boiling below 750° F. was subjected to viscosity reduction or cracking in a Cross cracking unit at a temperature of 850° F. and under a coil outlet pressure of 400 lbs. per square inch for a short period of time. The products of the cracking reaction were then cooled by indirect heat exchange under pressure with incoming charging stock and then passed into a flash drum maintained at 40 lbs. per square inch pressure where the more volatile materials produced in the cracking, such as the very light gasoline fractions and fixed gases are separated from the remaining residue. The cooling by heat exchange and the operation in the flash drum is preferably controlled so as to distill off the very light constituents of the cracked mixture and to retain fractions in the residue having a proper initial distillation point. Generally, I prefer to conduct the separation so as to leave a residue having an initial point of approximately 350 to 450° F. However, it is within the scope of my invention to retain fractions having even lower initial points such as, for example, the lighter gasolines having initial points of approximately 100° F. This material was then placed in storage.

For the sake of illustrating the peculiar characteristic of the bituminous cement as produced by the process forming the subject matter of my invention, the following tabulation is submitted which has been taken from inspection data on samples of the materials indicated in the table. The first column of figures represents the characteristics of the heavy road oil stock which was cracked, as described above, to reduce its viscosity and thus produce the bituminous cement of the second column of figures. The third column of figures represents a road oil having substantially the same content of 80 penetration asphalt as the bituminous cement produced by my invention, whereas the fourth column represents a road oil having approximately the same Saybolt furol viscosity at 122° F. as that of the bituminous cement. The last column of figures represents the characteristics of an "E" grade asphalt which has been cut back with approximately 26½ to 27% kerosene. This kerosene cut-back asphalt also contains approximately the same percentage of 80 penetration of asphalt as the cracked bituminous cement produced by my process. It will be observed that an "E" grade asphalt is a steam refined asphalt produced by steam distilling or topping an asphaltic crude oil residuum to vaporise the lighter fractions contained therein and to leave asphalt having a penetration at 77° F. of approximately 100 to 300, a melting point of 85 to 110° F. and a ductility at 77° F. of 100+ cm.

TABLE I

Comparison of characteristics of bituminous cement made by cracking a heavy road oil stock with the characteristics of conventional road oils and cut-back asphalt

Test	Heavy road oil stock	Bituminous cement by cracking heavy road oil stock	Ordinary road oil No. 1	Ordinary road oil No. 2	Kerosene cut-back asphalt
Gravity, ° A. P. I.	10.4	12.6	11.7	13.8	16.2
Flash point, ° F.	480	200	330	300	175
Percent of 80 penetration asphalt	82.0	74.9	73.7	58.0	74.0
Time to reach 80 penetration asphalt, hours	5	2½	6	9	3½
Viscosity, Saybolt furol at 122° F.	3,000	141	1,230	156	163
Viscosity, Saybolt furol at 210 ° F.	102	16	45	20	20
Distillation					
Initial, ° F.	650	422	622	555	435
Percent distilled at 437° F.	0.0	0.3	0.0	0.0	0.2
Percent distilled at 600° F.	0.0	7.0	0.0	0.0	20.5
Percent distilled at 680° F.	2.0	15.5	5.0	10.0	24.5
Test on Residue from Distillation					
Penetration at 77° F.	300+	300	300+	300+	194
Saybolt furol viscosity at 210° F.	105	67	51	26	270
Solubility in CS_2	99.8	99.8	99.8	99.8	99.8
Solubility in CCl_4	99.8	97.3	99.8	99.8	99.8

It will be observed from the above table that the bituminous cement or cut-back asphalt produced as above stated, will have a considerably lower Saybold furol viscosity at 122° F. and at 210° F. than Road Oil No. 1 of the table having substantially the same percentage of 80 penetration asphalt. In the case of the road oil the Saybolt furol viscosities at 122° F. and 210° F. are respectively 1230 seconds and 45 seconds as compared to 141 seconds and 16 seconds, respectively, for my bituminous cement. Road oils having substantially the same asphalt content as the bituminous cement produced by my process must necessarily be heated to high temperatures in order to permit efficient handling and application. In order to produce a road oil having substantially the same viscosities as the bituminous cement produced by my process, it will necessitate the use of a road oil having a smaller percentage of 80 penetration asphalt than the bituminous cement. Thus, Road Oil No. 2 having Saybolt furol viscosities at 122° F. and 210° F. of 156 and 20, respectively, which are slightly higher in viscosity than my bituminous cement will contain only 58% of 80 penetration asphalt as compared to substantially 75% of 80 penetration asphalt in my bituminous cement.

Consequently, the cementitiousness obtained from road oils is not as effective as the bituminous cement produced by my process. The time required to reach 80 penetration asphalt is considerably greater for the two road oils mentioned which are respectively 6 and 9 hours as compared to 2½ hours for the bituminous cement. By inspection of the distillation data, it will be observed that the bituminous cement contains a considerably higher percentage of fractions distilling at 437° F., 600° F. and 680° F. than the aforementioned road oils which, of course, makes my cement set much more rapidly than the road oils. It is generally known that substantially all oils boiling below 680° F. will evaporate from the bituminous cement or cut-back asphalt when applied on the road, or other places, in thin films or layers in approximately two months so that a distillation test at 680° F. is indicative of the amount of materials which are normally expected to evaporate from the bituminous cement when applied at its intended place of use, such as on the road.

The bituminous cement or cut-back asphalt is comparable with the kerosene cut-back asphalt indicated in the last column of the table. However, my bituminous cement is superior to the kerosene cut-back asphalt in that it requires less time to reach 80 penetration asphalt; it has a lower Saybolt furol viscosity at both 122° F. and 210° F. for even a higher asphalt content and it has a less total loss on the distillation test at 680° F. which indicates a higher percentage of asphalt remaining on the road per gallon of the cut-back asphalt applied. Also, it will be observed that the A. P. I. gravity of my bituminous cement is considerably lower than the kerosene cut-back asphalt for even a lower Saybolt furol viscosity. The bituminous cements produced by my process exhibit lower A. P. I. gravities for the same viscosities than ordinary cut-back asphalts which have been produced by dissolving an asphalt with a diluent such as kerosene.

One of the important advantages and characteristics of my bituminous cement over a kerosene cut-back asphalt which cannot be detected by an inspection of the laboratory distillation test is that my bituminous cement hardens better than the kerosene cut-back asphalt. This is probably due to the aromatic nature of the cracked diluent in the cement which has a higher evaporation tendency than is shown in the laboratory distillation test.

By controlling the penetration or viscosity of the asphaltic material before it is cracked, the extent to which the asphaltic material is cracked and the extent to which the cracked products are topped, a bituminous cement of almost any desired voltality and viscosity can be obtained. To illustrate the flexibility of my process to meet different requirements for rate of evaporation and development of cementitiousness, the examples in Table II are submitted which correspond to cracking a 175 penetration "E" grade asphalt under different lengths of time at a temperature of 860° F.

TABLE II

Tests of cracking 175 penetration "E" grade asphalt

	Run No. 1	Run No. 2
Production conditions		
Cracking time, minutes at 860° F.	3.4	6.06
Percent 250° F. E. B. P. gasoline distilled	6.0	7.3
Tests on product after removing 250° F. E. B. P. gasoline		
Gravity, ° A. P. I.	10.5	7.6
Viscosity, Saybolt furol at 122° F.	67	43
Flash point, ° F.	120	140
Fire point, ° F.	130	145
Percent of 80 penetration asphalt	72.4	77.7
Time to reach 80 penetration asphalt, hrs.	1¼	1
Distillation		
Percent distilled at 437° F.	5	3.5
Percent distilled at 600° F.	21.5	22.0
Percent distilled at 680° F.	27.5	29.0
Test on residue from distillation		
Penetration at 77° F.	115	42
Solubility in CS_2	98.46	94.79

It will be observed from Table II that the bituminous cement produced by cracking the "E" grade asphalt develops a high degree of cementitiousness upon evaporation as indicated by the distillation residue penetrations of 115 and 42 at 77° F. for the respective runs and that the cement has rapid curing properties as shown by the large amounts of distillate obtained in the usual distillation tests.

The process for producing the bituminous cement as described above is not to be restricted to the particular types of raw materials as given above, i. e. heavy road oil or asphalt. As cracking stocks, I may employ certain steam refined asphalts having melting points varying from 65 to 250° F. and also air-blown asphalts. The use of air-blown asphalts is advantageous when it is desired to produce a bituminous cement which will exhibit a minimum temperature susceptibility, i. e. minimum change in viscosity for change in temperature, upon evaporation of the diluent. Bituminous cements produced from air-blown asphalts by the methods described herein show less "bleeding" in hot weather and less brittleness in cold weather. I may also employ as cracking stock, the asphalt precipitated from asphaltic oils by means of such normally gaseous hydrocarbon solvents as liquid propane. This may be cracked to give a relatively low viscosity cement of high adhesiveness and cement value. Mixtures of bitumens and wax can be cracked to give products which contain less wax than the original mixture. In this regard, attention is particularly directed to the feasibility of cracking paraffin wax, such as that obtained by chilling a propane solution of oil containing wax to precipitate the wax from solution, to give a cracked product containing volatile fractions capable of acting as a diluent and then blending this cracked wax product or fraction thereof with the propane precipitated bitumen or asphalt. In this manner, a volatile bituminous cement would be obtained from wax and bitumen without necessity of cracking the bitumen.

While some of the common uses to which my cut-back asphalt or bituminous cement may be put comprise road building, preserving wood, painting metal, repairing roofs, etc., as stated hereinabove, I have found that the cut-back asphalt produced by my process is specially adapted as an adhesive or binding agent for the top surface of the mounds of tailings dump of copper or other mines to prevent erosion of the mound by the wind and rain. When these mounds dry out, a dry surface of dust remains which is carried by the wind over the surrounding communities, thus creating a nuisance. By spraying the surface of the tailings dump with the cut-back asphalt in amounts of approximately 1.5 gallons per square yard of surface, the asphalt will penetrate rapidly through the fine aggregate to such depth as to form an oiled shell of approximately one to one and one-half inches in thickness when the volatile cracked material has evaporated, thus leaving a satisfactory protection against the elements. The high asphalt content of the cut-back asphalt and good volatility resulting in development of remarkable cementitiousness and peculiar effectiveness in rapidly penetrating the tailings render the cut-back asphalt particularly suitable for this type of work.

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

Melting point	D–36–26
Penetration	D–5–25
Ductility	D–113–26T
Flash point, Cleveland open cup method	D–92–24
Percent of 80 penetration asphalt	D–243–26T

It is to be understood that the above description is merely illustrative of preferred embodiments of my invention of which many variations may be made within the scope of the following claims by those skilled in the art without departing from the spirit thereof.

I claim:

1. A cracked bituminous cement which is adapted for use as a road building, dust laying, wood preserving material or the like, said bituminous cement containing approximately 70 to 80% of 80 penetration at 77° F. of cracked asphalt and approximately 20 to 30% of cracked oil fractions, said cracked oil fractions in said bituminous cement being substantially free from fractions boiling below 400° F. and the major proportion of said cracked oil fractions boiling below 680° F.

2. A cracked bituminous cement which is adapted for use as a road building, dust laying, wood preserving material or the like which is produced by cracking an asphaltic crude oil residuum, said bituminous cement containing approximately 70 to 80% of 80 penetration at 77° F. of cracked alphalt and approximately 20 to 30% of cracked oil fractions, said cracked oil fractions in said bituminous cement being substantially free from fractions boiling below 400° F. but containing approximately 15% of cracked oil fractions boiling below 680° F.

3. A cracked bituminous cement which is adapted for use as a road building, dust laying, wood preserving material or the like which is produced by cracking an asphaltic crude oil residuum, said bituminous cement containing approximately 70 to 80% of 80 penetration at 77° F. of cracked asphalt and approximately 20 to 30% of cracked oil fractions, said cracked oil fractions in said bituminous cement being substantially free from fractions boiling below approximately 400° F. but containing approximately 15% of cracked oil fractions boiling below 680° F. and a substantial amount of cracked oil fractions boiling below 600° F.

4. A cracked bituminous cement which is adapted for use as a road building, dust laying, wood preserving material or the like which is produced by cracking an asphaltic crude oil residuum, said bituminous cement containing approximately 70 to 80% of 80 penetration at 77° F. of cracked asphalt and approximately 20 to 30% of cracked oil fractions, said cracked oil fractions in said bituminous cement being substantially free from fractions boiling below approximately 400° F. but containing approximately 15% of cracked oil fractions boiling below 680° F. and approximately 7% of cracked oil fractions boiling below approximately 600° F.

5. A cracked bituminous cement which is adapted for use as a road building, dust laying, wood preserving material or the like which is produced by cracking an asphaltic crude oil residuum, said bituminous cement containing approximately 70 to 80% of 80 penetration at 77° F. of cracked alphalt and approximately 20 to

30% of cracked oil fractions, said cracked oil fractions in said bituminous cement being substantially free from fractions boiling below approximately 400° F. but containing approximately 15% of cracked oil fractions boiling below 680° F. and approximately 7% of cracked oil fractions boiling below approximately 600° F. and said cracked bituminous cement having a Saybolt furol viscosity at 122° F. and 210° F. of 141 and 16, respectively.

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