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BITUMINOUS COVERING MATERIAL AND METHOD OF MAKING

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2 Sheets-Sheet 1

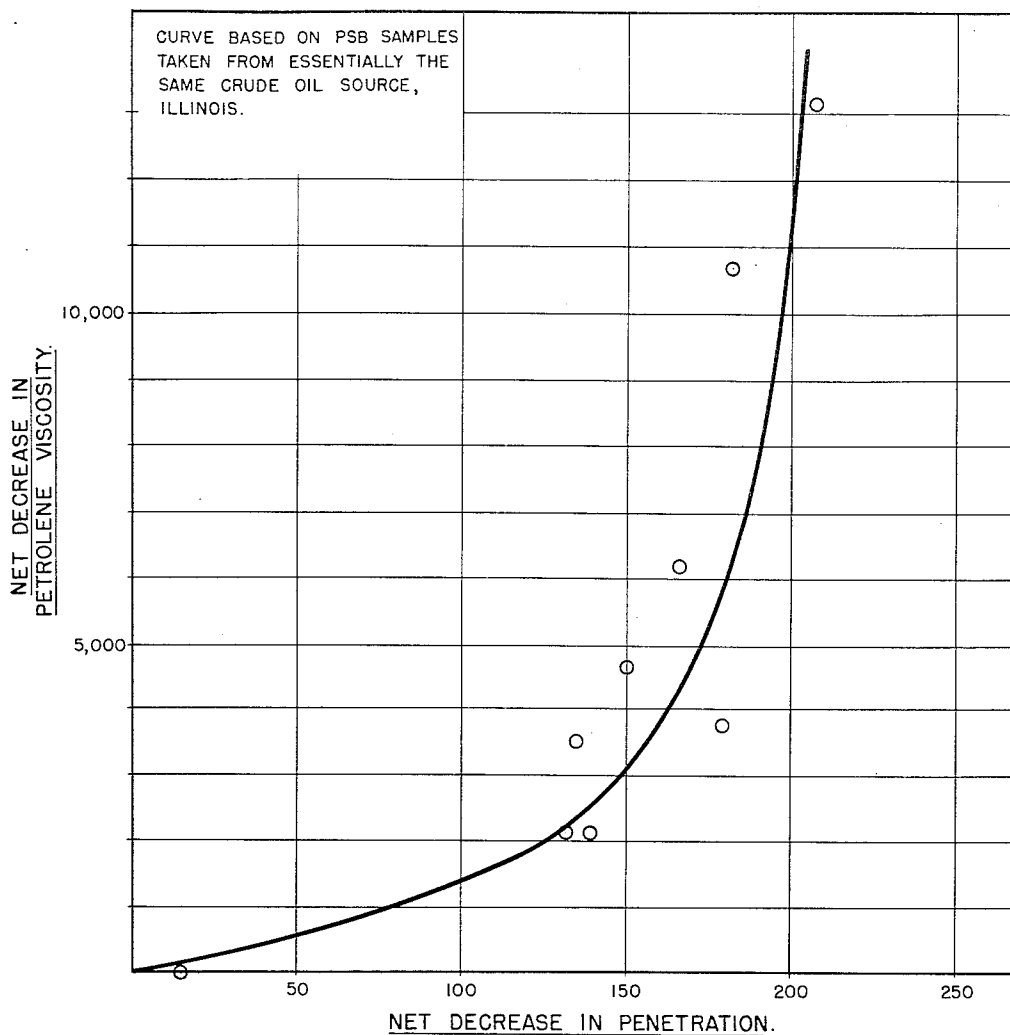


FIG. I.

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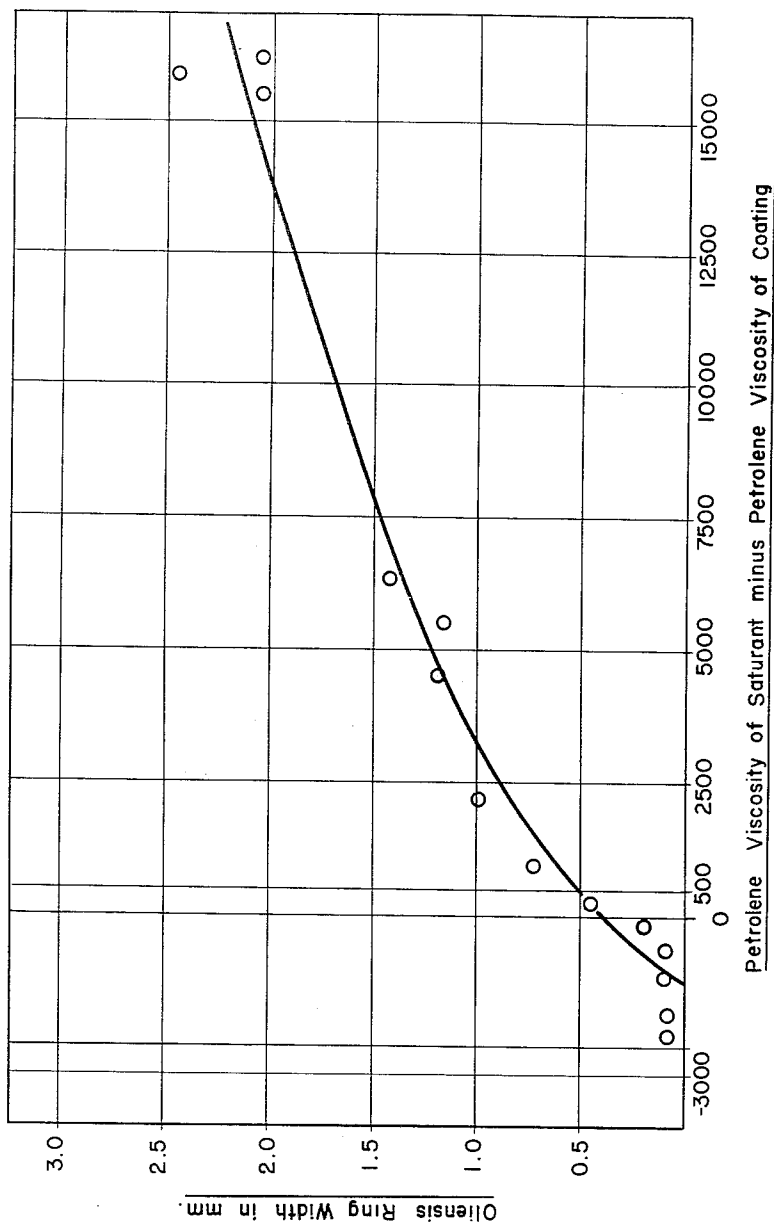


FIG. 2.

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BITUMINOUS COVERING MATERIAL AND METHOD OF MAKING

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10 Claims. (Cl. 117—92)

This invention relates to a new bituminous covering material consisting of two or more adjacent layers of bitumen of varying penetrations, and more specifically, to covering material in which the two or more adjacent layers of bitumen have adjusted petroleum viscosities.

In the production of certain bituminous covering materials, for example roofing asphalts, the "felt," an absorbent sheet material such as porous paper or other fibrous material is first saturated with a relatively soft asphalt known as the "saturant." One surface of the saturated felt is then coated with a relatively hard asphalt, known as the "coating." The coating may contain up to about 45% mineral filler such as finely ground limestone or silica in order to reduce the cost of the coating. Protective coatings for other applications such as those applied to underground pipes similarly involve layers of different asphalts.

One difficulty with these protective bituminous coatings is that brown stains or spots are occasionally found on the surface of the coating. Pfeiffer, "The Properties of Asphaltic Bitumen," page 256, Elsevier Publishing Company, Inc., New York, New York, 1950, reports that an oily layer forms at the interface of the saturant and the coating and this oil penetrates through pin holes in the coating giving rise to oily spots on the surface. This phenomenon is sometimes referred to as exudation. The presence of these stains or spots on roofing asphalt renders the product unsalable. Presumably, if the product were sold in this defective condition, the changes of which the staining are a symptom would tend to decrease the useful life of the product.

This staining problem has long been known and a number of suggestions have been made to overcome it. Most of the prior art processes result in hardening, i. e., decreasing the penetration of, the saturant. For example, Oliensis, G. L., "Exudation and Allied Reactions Between Bitumens," page 10, Forest Publishing Company, Forest Park, Illinois, 1949, reports the reduction of stains can be accomplished by more severe reduction of the pipe still bottoms in the vacuum stills, air-blowing the pipe still bottoms for a long period, or by cracking the pipe still bottoms to a slight extent by overheating. However, Oliensis makes no reference to the merits of these expedients with regard to the production of a good roofing material. It has been found that these expedients will so harden the ultimate roofing material that it will not possess the desired and requisite flexibility. Pfeiffer *supra*, reports that the staining effect can be eliminated by the addition of certain metal soaps or a larger quantity of heavily cracked bitumen to the saturant. These methods also result in products which do not have the desired and requisite flexibility.

Oliensis, G. L., "The Exudation Test for Bleeding in Bituminous Roofing," Ind. Eng. Chem., Anal. Ed., vol. 10 (1938), page 199, has developed a simple method of measuring the staining tendencies of any two adjacent layers of bituminous material. It essentially consists of placing a $\frac{1}{16}$ " diameter drop of a saturant on the talc

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dusted surface of a coating for 72 hours at 110° F. The width of the black ring of discolored talc, that forms about the drop is a measure of the staining tendency. If this width does not exceed $\frac{1}{2}$ millimeter, the asphalt roofing made from the saturant and coating will be acceptable.

It is an object of this invention to provide an improved compatible bituminous covering material in which the staining or exudation of the saturant into the coating is substantially eliminated.

It is a further object of this invention to provide a method for the production of a compatible bituminous covering whereby a uniform, non-staining product may be obtained.

Asphalt is considered as consisting of two major components, asphaltenes and petroleues. The term "asphaltene" as used herein refers to that portion of an asphalt which is insoluble in 50 volumes of normal pentane per volume of asphalt. Asphaltenes are the micelles of a colloidal system which are insoluble in low molecular weight organic solvents such as pentane, aromatic-free gasoline and ether. The asphaltenes are more aromatic than other petroleum fractions, generally speaking. Because of the characteristic lattice structure of the high molecular weight asphaltenes, I concluded that it was not likely that the asphaltenes would migrate nor cause the other components to do so.

Petroleues are liquids of molecular weight from 400 to 900 and of widely varying aromatic content. The term "petroleum" is used herein to refer to that portion of asphalt which is soluble in normal pentane. Since staining is the migration of the lighter components or oily constituents of asphalts from one medium to another, I conceived that the migration was caused by some difference in the liquid constituents in the two asphalt layers. I have now discovered that the migration is from the petroleum fraction and that it can be eliminated if the adjacent layers of bitumen possess petroleum fractions having certain related viscosities. More particularly, the petroleum viscosity of the saturant must not be substantially more than the petroleum viscosity of the coating. The petroleum viscosity of the coating may always be greater than the petroleum viscosity of the saturant, but for reasons that will appear hereinafter, this is not ordinarily the situation and the manufacturing process is generally one of bringing the petroleum viscosity of the saturant and the coating to such a relationship that the petroleum viscosity of the saturant is not substantially more than that of the coating.

A typical saturant may have the following properties:

Melting point (R. & B.), 100–150° F.

Pen. at 77° F., 220–40

Per cent asphaltenes, 13–24.5

This saturant is generally applied at a temperature of around 400° F.

Typical specifications of a coating asphalt (excluding any filler) are:

Melting point (R. & B.), 210–235° F.

Pen. at 77° F., 25–10

Per cent asphaltenes, 35–45

The fixing of the petroleum viscosity in accordance with the invention will not necessarily preclude the use of asphalts having different penetrations. The characteristics of any particular asphalt are determined by two primary independent variables: (1) the relative proportions of asphaltenes and petroleues, i. e., the percentage asphaltenes, and (2) the viscosity of the petroleum fraction. The latter may be adjusted as is explained hereinafter.

If the petroleum viscosity is the same in both layers, for

example, then only the percentage of asphaltenes (relative proportions of asphaltenes and petroleues) is varied to achieve a difference in penetration. In this manner, the layers of bitumen of different penetrations can be obtained and the staining problem eliminated.

Another factor that is involved in determining the characteristic of asphalt is the viscosity gravity constant. This is a measure of the aromaticity of the petroleues and is controlled primarily by the source of the crude from which the asphalt is made. Since generally the coating and saturant will be made from asphalt from a single crude source, or from crudes not having widely different properties, it is practical to eliminate this factor from consideration in further describing the invention.

The proportion of asphaltenes may be varied by reduction and/or oxidation of pipe still bottoms. These constitute the residuum of the crude after the volatile fractions have been removed by distillation. Except at temperatures where cracking may begin, the reduction of pipe still bottoms in a vacuum tower, for example, is accomplished by the removal of the petroleues of lower viscosity and, therefore, is characterized by an increase in the asphaltene content and the petrolene viscosity of the remaining pipe still bottoms. This is one way in which the amount of asphaltenes may be adjusted, but if the viscosity of the petrolene fractions is not that desired it must be adjusted by other means.

In the oxidation of pipe still bottoms, petroleues are converted to asphaltenes. However, in this oxidation the heavier fractions of the petroleues are more easily converted, and the oxidation product is characterized by petroleues of decreased viscosity. The magnitude of this change is illustrated in Fig. 1 of the drawing.

Petrolene viscosities and penetration values of various pipe still bottoms and asphalt samples from the same crude oil source, both before and after oxidation, were determined by plotting their respective differences. It is to be noted from the values plotted in Fig. 1 that small reductions in penetration are accompanied by relatively small decreases in petrolene viscosity. As the degree of oxidation is increased, however, the reduction in petrolene viscosity increases quite rapidly.

As illustrative of this difference, pipe still bottoms having a penetration at 77° F. of 200-300 and a petrolene viscosity of 10,000-15,000 poises may be highly oxidized to make a hard coating. The melting point would be raised to 220° F., and the petrolene viscosity would be reduced to 3,000 poises. On the other hand, if the saturant were made from these same pipe still bottoms, the amount of oxidation to make the relatively soft asphalt saturant would not be large and there would not be any substantial reduction in the petrolene viscosity, i. e., it would remain about 10,000-15,000 poises. The marked difference between the petrolene viscosities of these two fractions would account for the poor results, if they were used. In order to avoid this, it is necessary to make some adjustment.

The respective properties of the saturant and coating may be adjusted in accordance with this invention by blending them with a heavy oil distillate such as cylinder stock derived from the same crude oil source. For example, the portion of pipe still bottoms used in making the saturant might be blended with cylinder stock to give a lower petrolene viscosity before oxidation. A distillate consisting essentially of petroleues of any desired viscosity may also be blended with either or both fractions in order to obtain any desired degree of variation in the petrolene viscosities of the asphalts. Other blending agents such as "wax slops" may also be employed.

Another way of accomplishing this involves reducing the pipe still bottoms to different extents before oxidation. For instance, pipe still bottoms may be oxidized slightly to provide a penetration of about 190 to produce the saturant. The pipe still bottoms used in making the coating would be reduced further before oxidation so as

to eliminate the light viscosity petroleues. The relative proportion of asphaltenes would be increased during the reduction and the amount of oxidation necessary to make a low penetration asphalt would be less. Upon oxidation, therefore, the viscosity of the petroleues would not be so drastically reduced.

The following examples are illustrative of the invention:

Example 1

(a) The same pipe still bottoms were employed in this and in all of the other examples. It was converted to a saturant having a melting point (R. & B.) of 102° F., a penetration at 77° F. of 199 and a petrolene viscosity at 77° F. of 16,890. A coating was made by oxidizing the pipe still bottoms to a melting point (R. & B.) of 220° F., a penetration at 77° F. of 8, and a petrolene viscosity at 77° F. of 3,192. When this is tested by the method described heretofore, the Oliensis ring width is 1.0 mm. It is to be noticed that the difference in petrolene viscosity of the saturant and coating is approximately 13,700. This shows that with this wide difference in petrolene viscosities the product does not pass the Oliensis test described heretofore.

(b) When the saturant is 85% of the pipe still bottoms and 15% of wax slops having a Saybolt viscosity at 210° F. of 81.9 sec., and a pour point of 70° F., oxidized to a melting point (R. & B.) of 108° F., a penetration at 77° F. of 131, and a petrolene viscosity at 77° F. of 3,080, and the coating is the same as described above, the product had an Oliensis ring width of 0.10. In this case, where the petrolene viscosities of the saturant and coating were approximately the same, the product passed the Oliensis test.

(c) When the saturant is 70% pipe still bottoms and 30% cylinder stock having a Saybolt viscosity at 210° F. of 209.5 sec., and a pour point of 65° F., oxidized to a melting point (R. & B.) of 101° F., a penetration at 77° F. of 240 and a petrolene viscosity at 77° F. of 2,040, the product had an Oliensis ring width of 0.1. In this instance the petrolene viscosity of the coating is substantially more than the saturant, and the product passed the test.

Example 2

(a) As another example of the invention, the saturant is the same as in Example 1(a) and the coating was prepared from 92% of the same pipe still bottoms and 8% of the same cylinder stock as in Example 1(c) oxidized to a melting point (R. & B.) of 226° F., a penetration at 77° F. of 11, and a petrolene viscosity at 77° F. of 1,425. The difference between the petrolene viscosity of the saturant and the coating is 15,475 and the product had an Oliensis ring width of 2.0 mm., showing its unacceptability.

(b) With the same coating, however, and with a saturant made from 70% of the pipe still bottoms and 30% of the wax slops oxidized to a melting point (R. & B.) of 104° F., a penetration at 77° F. of 183 and a petrolene viscosity at 77° F. of 1,320, the product had an Oliensis ring width of 0.1 mm. showing the complete acceptability of the product when the petrolene viscosity of the saturant and the coating is substantially the same.

Example 3

A saturant was made from the residuum of a pipe still feed distilled to 525° F. at 0.01 mm. in a pot still and oxidized to a melting point (R. & B.) of 105° F., a penetration at 77° F. of 165, and a petrolene viscosity at 77° F. of 950. The coating was made from 65% of the pipe still bottoms and 35% of the cylinder stock oxidized to a melting point (R. & B.) of 218.5° F., a penetration at 77° F. of 17, and a petrolene viscosity at 77° F. of 730. The product formed had an Oliensis ring width of 0.17, showing that the difference in petrolene viscosity of 220 is not excessive.

Example 4

A sample of pipe still bottoms from an aromatic type crude was divided into two parts. The first part was oxidized to a melting point (R. & B.) of 105° F., a penetration at 77° F. of 170, and a petrolene viscosity at 77° F. of 2650, to produce a saturant.

The second part was reduced in a vacuum tower to remove a portion of the more volatile petrolenes and was then oxidized to provide a coating material having a melting point (R. & B.) of 221° F., a penetration at 77° F. of 10, and a petrolene viscosity at 77° F. of 2270. The difference between the petrolene viscosities is within the permissible range and when the roofing material was prepared using this saturant and coating, it was found that there was no stain of the saturant into the coating.

The above examples show that if the petrolene viscosity of the coating is more than the petrolene viscosity of the saturant there is no problem of exudation. While the ideal situation would appear when the petrolene viscosity of the two components is the same, I have found that the petrolene viscosity of the saturant may be slightly higher than that of the coating without exceeding the limits set in the Oliensis test. As can be seen from Fig. 2 the petrolene viscosity of the saturant may be up to about 500 poises more than the petrolene viscosity of the coating before the limits of the test are exceeded.

It will be obvious to those skilled in the art that many modifications may be made within the scope of the present invention without departing from the spirit thereof, and the invention is to be restricted only in accordance with the appended claims.

The term "coated" as used in the claims is inclusive both of surface coatings and of impregnating coatings up to and including saturating coatings.

I claim:

1. A bituminous covering comprising an absorbent sheet material saturated with a first asphalt, said asphalt saturated sheet being coated with a second asphalt harder than said first asphalt, the petrolene viscosity of the saturant at 77° F. being not more than about 500 poises more than the petrolene viscosity of the coating at 77° F.

2. A bituminous covering comprising a porous paper in sheet form saturated with an asphalt having a melting point of about 100° to about 150° F. and a penetration at 77° F. of about 220 to about 40, and having a coating thereon of an asphalt having a melting point of about 210° to about 235° F. and a penetration at 77° F. of about 25 to about 10, the petrolene viscosity of the saturant at 77° F. being not more than about 500 poises more than the petrolene viscosity of the coating at 77° F.

3. The process of making a covering which comprises

saturating an absorbent sheet material with a first asphalt and coating it with a second asphalt harder than said first asphalt, the petrolene viscosity of the saturant at 77° F. being not more than 500 poises more than the viscosity of the coating at 77° F.

4. The process of claim 3 in which the petrolene viscosity of the saturant and the coating is substantially the same.

5. In a bituminous covering the combination comprising a first asphalt layer having a melting point of about 100° to about 150° F. and a penetration at 77° F. of about 220 to about 40, one side of said first asphalt layer being coated on a base and the other side having in contact therewith a second layer of an asphalt having a melting point of about 210° to about 235° F. and a penetration at 77° F. of about 25 to about 10, the petrolene viscosity of the first layer being not more than about 500 poises at 77° F. more than the petrolene viscosity of the second layer.

6. A process of making a covering which comprises applying to a base coated with a first asphalt and in contact with the first asphalt a second asphalt harder than the first asphalt, the petrolene viscosity of the first asphalt at 77° F. being not more than 500 poises more than the viscosity of the second asphalt.

7. A process in accordance with claim 6 in which at least one of said asphalts comprises a heavy distillate in an amount to modify the petrolene viscosity of the asphalt.

8. A process in accordance with claim 6 in which the second asphalt is an oxidized asphalt.

9. A process in accordance with claim 6 in which the second asphalt is a vacuum reduced and oxidized asphalt.

10. A bituminous covering comprising a base coated with a first asphalt which itself is coated with a second asphalt harder than the first asphalt, the petrolene viscosity at 77° F. of the first asphalt being not more than about 500 poises more than the petrolene viscosity of the second asphalt.

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