

March 13, 1956

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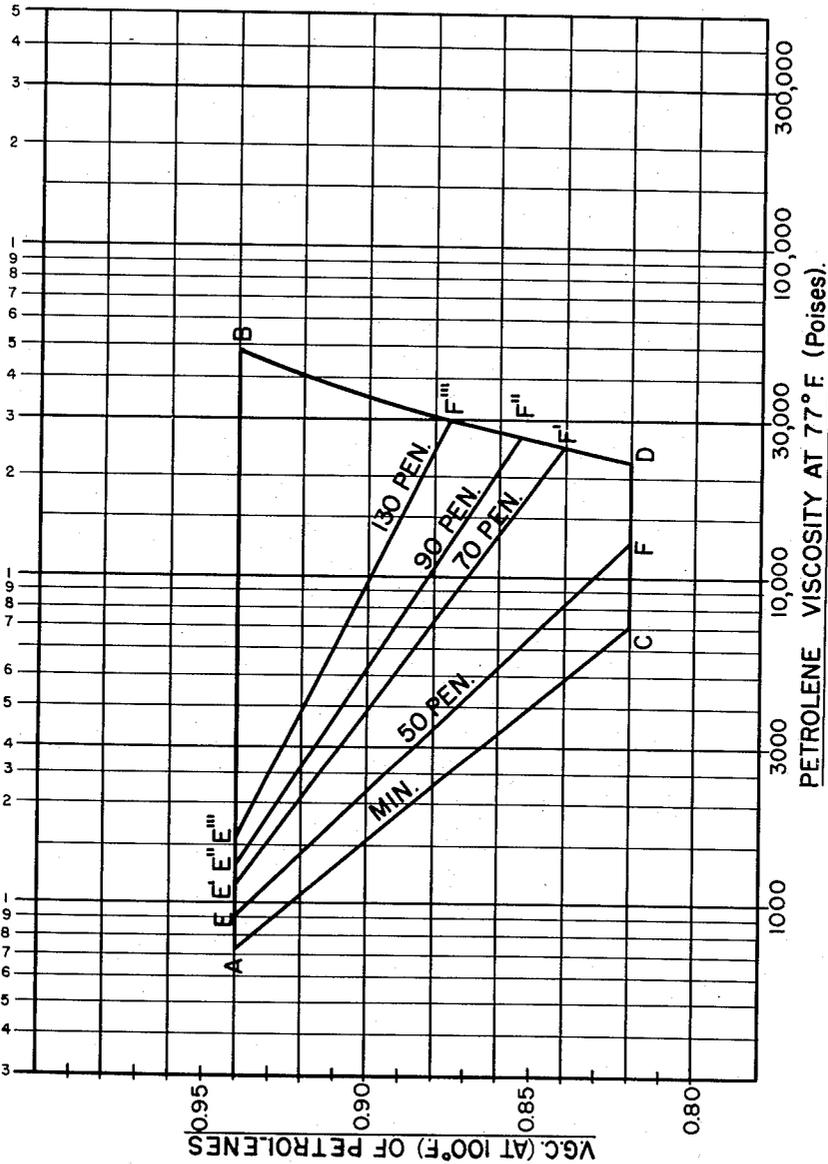
2,738,312

PREPARATION OF ASPHALTIC MATERIAL

Filed June 11, 1952

2 Sheets-Sheet 1

FIG. 1.



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2 Sheets-Sheet 2

FIG. 2.

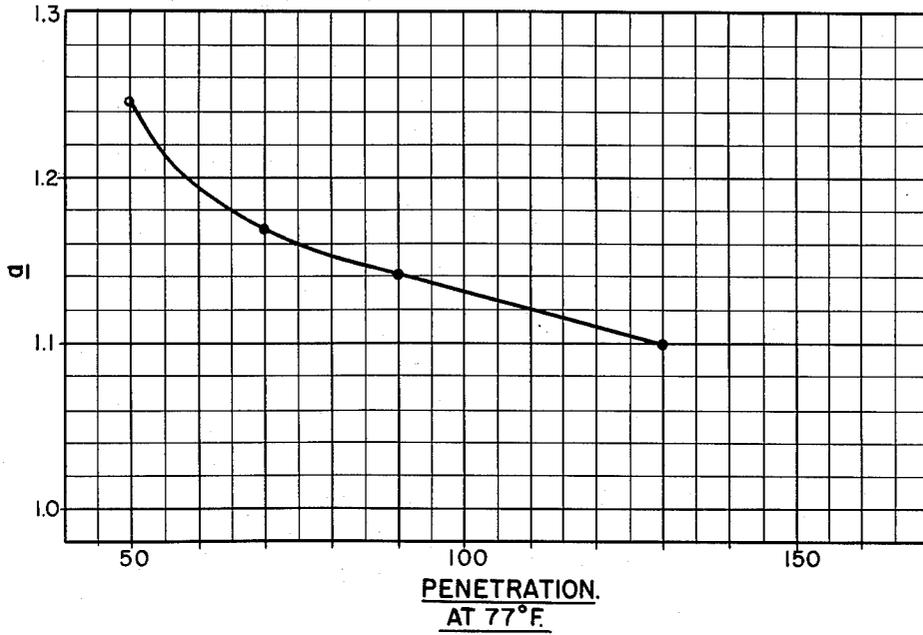
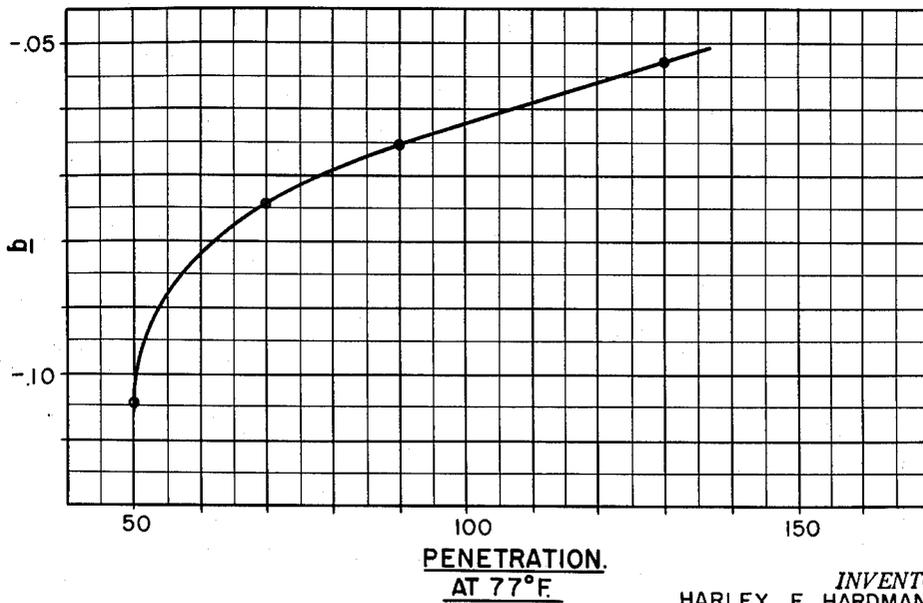


FIG. 3.



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2,738,312

**PREPARATION OF ASPHALTIC MATERIAL**

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2 Claims. (Cl. 196-74)

This invention relates to an improved process for producing bituminous compositions having improved flow properties and softening point relationships. More particularly, the present invention relates to an improved process for predetermining and controlling the preparation of bituminous compositions having greater stability and serviceability.

Particularly in the utilization of asphalt compositions for road paving material, it is important that the composition employed have suitable flow properties. If an asphalt pavement were rigid and subjected to a decrease in temperature amounting to 30° F. between the surface and the bottom, the internal stresses at the bottom of the pavement would be of the order of 300 lbs. per square inch and the paving would crack. In order to prevent cracking, the internal stresses must relax. Since the mineral aggregate contained in the paving composition is unyielding, stress relaxation must occur through a flow of the asphalt. Bituminous pavements must also possess the ability to undergo deformation, that is, bending without breaking in transmitting traffic loads to the pavement foundation and to the natural subgrade. Thus, a bituminous pavement may be regarded as an abrasion-resistant, weather impervious, protective coating for the foundation which actually supports the traffic load.

With the development of the extensive use of asphalt cements in bituminous pavements, asphalts have been extensively investigated and a number of specifications have developed over the years. As more and more information has accumulated, additional specifications have been added from time to time to the growing list. Among the numerous specifications which are frequently required of asphaltic material for paving purposes are no-foaming tendencies at elevated temperatures, prescribed values of specific gravity, flash point, percent loss at elevated temperature, penetration of residue, total bituminum content, percent ash content, negative oliensis spot test, softening point, ductility at 77° F., temperature susceptibility and penetration at 77° F. Of these, the most rigidly required are the latter four, that is, the softening point, ductility, temperature susceptibility, and penetration.

A sample specification table is given below for various penetration grade asphalt cements:

**TABLE**

Grade.....	50/60	60/70	85/100	120/150	200/220
Pen., 77°-100 g.-5 sec.	50-60	60-70	85-100	120-150	200-220
Pen., 32°-200 g.-60 sec.	15-15	18	20	25	32
(Min)					
Temp. Sus., Pen., 77°/Pen. 32° Max.	3.3-4	3.3-3.9	4.2-5.0	5-6	6.3-6.9
Ductility, 77°-5 cm./Min. (Min)	110	110	110	110	110
Soft. Pt. R. & B., ° F.	120-135	115-130	110-120	100-110	90-105
Oxidation, cc. 0.1 N KMnO <sub>4</sub> (Max.)	2.0	2.0	2.0	2.0	2.0

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The present invention relates to a process for the manufacture of high quality paving asphalts having viscosity gravity constants (V. G. C.), at 100° F. of petrolenes, in the range 0.82-0.94, and petrolene viscosities, at 77° F., within the overall operating area ABCD of Figure 1. Products having these values will meet the specifications of the table, and will also exhibit the desired characteristics and properties of low temperature behavior, resistance to oxidation, bleeding, and resistance to deleterious action of water.

The softening point is a standardized test for identifying different grades of asphaltic material. It is especially useful in ascertaining the adaptability of a bituminous material for certain definite usages, such as its resistance to the sun or artificial heat. The most usual test is the standardized ring-and-ball method defined in American Society for Testing Materials (ASTM) Standards 1942, II, 488.

The ductility of a bituminous material represents its capacity for elongating or stretching. The ductility test is useful for determining the adaptability of bituminous materials for paving purposes. Ductility is measured by the method described in ASTM Standards 1942, II, 466 and is essentially a measure of the distance a briquette, of prescribed dimensions, of bituminous material will elongate before breaking when its ends are pulled apart at a specified speed and at a specified temperature.

Temperature susceptibility is a comparison of the consistency or hardness of the asphalt at elevated temperatures with its consistency at lower temperatures. Numerically it is the ratio of the penetration value of the asphalt at a higher temperature to the penetration of the asphalt at a lower temperature. Several different higher temperatures and several different lower temperatures have been proposed as the best for comparison purposes. For purposes of the present disclosure the two values are taken at 77° F. and 32° F., respectively. The temperature susceptibility is therefore defined herein as the ratio of the penetration at 77° F. divided by the penetration at 32° F.

Penetration is defined as the consistency of a bituminous material, that is, the resistivity to deformation, and is expressed as the distance that a standard needle vertically penetrates a sample of the material under known conditions of loading, time and temperature.

Oxidation stability is measured by the volume of 0.1 N potassium permanganate solution consumed by a 0.02 gram sample film. The procedure for conducting this measurement is described in detail by Hveem, F. N., Proc. Assoc. Asphalt Paving Tech., vol. 15, 129-130 (1943).

Unfortunately, however, these specifications which are generally required can be made with asphaltic materials which are still not satisfactory for paving purposes. In addition to the many usual specifications, there are also several other properties which are known to affect the service life of asphaltic materials for paving purposes. It is desirable therefore to have some means of determining in advance or of controlling these properties of asphaltic materials as well as the more conventional specifications. These properties are related to low temperature behavior, resistance to oxidation (weathering), bleeding and resistance to deleterious action of water (stripping).

Failure of asphalt paving is often attributable to the excessive brittleness of the asphalt at low temperatures. This failure is most commonly observed in the deterioration of sections of the pavement during the winter and early spring months and is evidenced by cracks appearing in the paving surface. To avoid this failure a satisfactory asphalt material must maintain its ability to flex

and absorb heavy loads without cracking at low temperatures.

Also pavements fail if, for any other reason, they become too hard and brittle. Such hardening may occur slowly over several years from oxidation by the air. Thus it is important also that asphaltic materials be resistant to oxidation after they are applied to the pavement surfaces.

Another important cause of the failure of asphalt pavements is that of "bleeding" which is accelerated and most generally observed during seasons of higher temperatures. This effect is apparent in the exudation of oil which collects on the surface of the pavement in a greasy film. Visual evidence of "bleeding" is afforded by a lack of gloss and streaking when the asphalt surface is lightly wiped. It is very desirable to prevent the bleeding of the asphaltic material in order to avoid slippery conditions of the pavement surfaces.

Still another serious cause of pavement failure which is unrelated to the foregoing causes is stripping by water. This is particularly prevalent in areas where ground or surface waters remain in contact with the asphalt-containing layer of the pavement. The failure may be explained by the asphalt films which bind together the stones being slightly displaced and floating away, leaving loose stone. The action usually starts on the underneath side of the pavement and progresses upwardly resulting finally in pot-holes through the entire pavement. Thus it is highly desirable to produce an asphaltic material having the indicated desirable characteristics.

Heretofore it has not been possible to predict with any degree of certainty the serviceability and lasting characteristics of any batch of asphaltic material designed for paving purposes. Actual results of various prepared stocks of asphalt have been hard to determine because in a particular stretch of asphaltic pavement, the material which is applied will no doubt consist of a mixture of individual batches of asphaltic material prepared under differing conditions. It has now been found, however, that asphaltic materials prepared under specific conditions as hereinafter described will provide an asphaltic composition which will possess desired characteristics in the indicated properties.

It has now been found that if the refining of asphalts is so controlled that the viscosity of the petrolene fraction of the refined asphalt is within a certain range and the asphalt is selected with attention to its basic nature, all as explained hereinafter, the asphaltic material will display improved characteristics in the desired properties.

It is, therefore, an object of the present invention to describe a method for controlling the preparation of asphaltic material to obtain desired characteristics.

Still another object is to provide a uniform bituminous paving material having desired service properties.

Another object is to provide a uniform bituminous paving material of desired low temperature, oxidation, bleeding and stripping properties.

Other objects will be apparent to those skilled in the art from the following detailed description of the process and improved bituminous products.

Asphaltenes and petrolenes are components of asphalt. The term "asphalt" is used herein to apply to both native asphalts and pyrogenous asphalts. Native asphalts include asphalts occurring naturally in a pure or fairly pure state or asphalts associated naturally with a substantial proportion of mineral matter such as sand, sandstone, clay, etc., which can be separated from the asphalt by solvent extraction methods. Pyrogenous asphalts include residues obtained from petroleum by various means such as distillation (e. g. still bottoms or residual oil), blowing (e. g. blown asphalts, etc.). Asphalts are considered to be colloidal systems in which asphaltenes constitute the dispersed phase and petrolenes the dispersing phase. The term "asphaltene" as used herein refers to

that portion of an asphalt which is soluble in carbon disulfide and insoluble in 50 volumes of normal pentane per volume of asphalt. The term "petrolene" is used herein to refer to that portion of asphalt which is soluble in normal pentane.

Asphalts are frequently identified by the nature of the asphaltic residue itself or by the nature of the crude from which it may be derived. An indication of its nature is provided by a numerical value designated as its viscosity gravity constant which is related to its specific gravity. Petrolene viscosity gravity constant (V. G. C.) is fixed by the crude source from which the asphalt is obtained. This V. G. C. is a convenient means of measuring the molecular structure of the asphaltic material and has been defined by Hill and Coates Ind. Eng. Chem., 1928, page 641. Low V. G. C. values indicate a larger proportion of paraffinic material and high V. G. C. values indicate larger concentrations of aromatics and naphthalenes. Thus, a value of 0.8 indicates an extremely paraffinic asphalt and a value of 0.9 indicates a correspondingly large concentration of aromatics and naphthalenes.

Petroleum asphalt may be defined as the residual fraction of crude oil whose lighter fractions have been removed by distillation. The asphalt possesses certain empirical characteristics which, in turn, are determined by the intended use of the asphalt. The production of asphalt from crude oil is almost universally controlled by allowing the distillation process to continue until the consistency of the asphalt reaches a predetermined value which is specified for the particular use to which the asphalt is to be applied. As already pointed out, this consistency is defined as the "penetration" of the residue.

A desired penetration value for the final product may be obtained by either a straight distillation to the desired consistency, or by the combination of distillation to a certain consistency followed by oxidation of the product to the finally desired consistency or penetration. Thus, a penetration value of 70-80, for example, may be obtained either by distilling a crude oil completely to a penetration of 70-80 or by distilling the crude oil to some intermediate penetration, such as 200-300, and then by oxidizing this residue until the penetration value is decreased to the desired 70-80.

Asphalts of differing characteristics may result by obtaining the desired penetration value by the different procedures of distilling completely to the desired penetration value or by distilling only part way and oxidizing until the desired penetration is obtained and also differing characteristics may be realized by distilling to different penetration levels, followed by oxidation of the residues to the same final penetration value. Asphalts of varying characteristics are also obtainable by preparing asphalts of two penetration grades, one hard and one soft, by straight distillation. Various paving grade asphalts are then prepared by blending the two in suitable proportions.

The oxidation of the reduced crude, which is a commonly employed mode of operation, is usually effected by blowing air through the residue at a temperature of about 400 to 500° F. at a rate of about 30 to 50 cubic feet per minute per ton of asphalt charge until the desired penetration is obtained.

The petrolene viscosity of the petrolene fraction decreases slightly during oxidation and this factor is accommodated in the minima set forth below. The petrolene viscosity gravity constant, which is indicative of the molecular structure and nature of the asphalt, is not substantially altered by the oxidation of the crude residue.

In employing the asphaltic material in the preparation of paving, one of two methods is employed. The asphaltic material, which is generally denoted as asphalt cement, may be heated to a temperature at which it is molten, mixed with a quantity of loose rock, and spread upon a prepared road bed where it cools to a solid layer of rock bound together with the asphalt cement. In another method of binding the asphaltic material, the asphalt may

be softened or liquefied by the addition of petroleum distillates and, in this form is denoted as "cut-back" asphalt. This cut-back asphalt may then be applied to the surface of the road bed and a thin layer of fine rock scattered uniformly over the fresh asphalt or the procedure may be reversed and the liquefied asphalt sprayed over a thin layer of finely divided rock. An attribute of this cut-back asphalt is that it exhibits rapid adhesion to the rock and that the solvent evaporates fairly readily to leave the solid layer of rock and asphalt cement. The present invention is applicable to both forms of asphaltic material, that is, asphalt cement and cut-back asphalt.

It is well known that asphaltic materials for paving purposes should be of a particular nature. An indication of the nature of the asphalt is supplied by its V. G. C. rating described above.

The use of cracked residue or stock for asphalt making has been practiced to only a limited extent since the cracked materials are inferior to uncracked products from the standpoint of weathering and durability.

An excess of paraffin wax reduces the effective life span of an asphaltic product by lowering ductility and adhesion and increasing susceptibility to temperature changes. Also, residual oils derived from semi-asphaltic or non-asphaltic petroleums must be blown longer to obtain a product of the same fusing-point, and the blown asphalt is likely to appear quite oily and greasy. Further, on cooling, paraffin wax in bitumen has a tendency to concentrate at the surface. This concentration of paraffin wax at the surface of the bitumen reduces the tackiness of the latter.

In the preparation of asphalt for paving purposes, there has long been a need for a scientifically controlled method of control which would ensure a uniform product of long service life. Not fully appreciating all the variables which govern the properties of any given asphaltic product, manufacturers have relied largely upon obtaining a product of the specified penetration value and using what information they had by way of past experience to provide that the product also met other specifications. Thus they have had to rely, among other things, upon a selection of crude stock from which to recover asphaltic material, upon experimentation and various combinations and methods of obtaining the desired penetration values and upon blending of various batches of asphaltic products to provide the asphalts which would meet the specifications for different consumers and purposes. Securing a product with suitable penetration value was no assurance that it would meet all specifications for paving purposes, and even if it met all specifications there was no absolute guarantee that the product would display uniform serviceability. It was found that the important properties of low temperature behavior, weathering, bleeding, stripping, etc. may vary considerably for two different asphaltic materials having the same penetration value and meeting the usual specifications. Hence, a method of preparing asphalts by which these other important properties may be controlled has been greatly needed. Such a control in the preparation of satisfactory asphalts has been discovered and is described herein.

On examination of a number of bituminous paving failures as exhibited by cracks and pits developing in the paving, it was determined that the cause of failure resulted from the inability of the asphalt to flow or to deform under both thermal (climatic) and traffic stresses. Thus the failures were related to poor flow properties. It has been developed by E. Thelan, J. Applied Phys., 8,135 (1937), C. Mack, J. Soc. Chem. Ind., 53,306 (1939), C. Mack, Proc. Assoc. Asphalt Paving Tech., 13,198 (1942), and others that the flow properties of asphalts from varying crude sources could be expressed by the equation

$$n = \frac{1}{1+S}$$

where S is the slope of a curve of the logarithm of the viscosity of the asphalt plotted against the logarithm of the rate of shear of the asphalt.

It has been further determined that each of the more important specifications are directly related to "n" and the value of "n" changes with variations in the value of any of the properties.

For desirable asphalts for paving purposes the value of "n," to satisfy a minimum ductility of 100, has been found to be less than 1.6. To satisfy the specifications for softening point, the value "n" is found to be within the range of about 1.3 to 1.6. For satisfactory temperature susceptibility, "n" must be between about 1.3 and 1.6. Thus the limits of "n," to satisfy specifications of softening point, ductility and temperature susceptibility, must be between 1.3 and 1.6. These limits can be theoretically developed and are verified experimentally.

The relationship between "n" and the above properties of the asphaltic material is as follows. As "n" increases, the softening point also increases but the ductility and the temperature susceptibility decrease.

The value of "n" is also found to be related to the petroline viscosity of the asphalt in a manner such that as the petroline viscosity increases the value of "n" decreases. Thus, changes in the value of "n" may indicate alterations in one of the properties of softening point, ductility, temperature susceptibility or petroline viscosity and conversely, a change in one of these properties will be reflected in a change in the value of "n" for that asphaltic composition.

The change of "n" with changes of petroline viscosity is similar to the changes of the values of "n" for changes in softening point, ductility and temperature susceptibility, respectively. Thus it is seen that changes in the value of the petroline viscosity affect the value of "n" and thereby the values of the latter properties of the asphaltic material. There is then, a relationship between values of petroline viscosity and values of softening point, ductility and temperature susceptibility, respectively.

Further, it was determined that the factors which affect the softening point, ductility and temperature susceptibility are the three independent variables (a) weight percent of asphaltenes; (b) petroline viscosity, generally measured at 77° F.; and (c) petroline viscosity gravity constant (V. G. C.) (herein I have used the 100° F. V. G. C.). All other variables such as molecular weight of the petrolenes and asphaltene, aromaticity of asphaltenes, C/H ratio, etc. are found to be related to one or more of the above three variables. Aside from the composition, which governs a number of the characteristics of the asphaltic product, the consistency or hardness is separately defined by the penetration value. There is one correlating equation for penetration and one for "n." The correlating equation for penetration (P) is as follows:

$$P = 117.5 + 631,500X^{-2.99} + 128.1Y^{1.85} - 56.9 \log Z$$

where X is the weight per cent asphaltenes, Y is the 100° F. petroline viscosity gravity constant, and Z is the petroline viscosity at 77° F.

The correlating equation for "n" is as follows:

$$n = \frac{A}{-1.10 + 1.018A}$$

where  $A = -5.22 + 49.0X^{-0.916} + 7.41Y^{6.82} + 1.37Z^{0.0896}$  where X, Y and Z are as defined above.

Both of the equations involve four variables. Thus, a given penetration may be obtained at an infinite variety of compositions, each of which will have a different "n." The present invention provides a method whereby those compositions having optimum "n" values, and the other enumerated desirable properties which are also dependent upon composition, may be uniformly obtained.

From the foregoing discoveries, it is seen that the properties of asphalt may be considered as a four-component system which is governed by the values of the

(1) penetration, (2) weight percent of asphaltenes, (3) petrole viscosity and (4) petrole viscosity gravity constant. Arbitrary choice of any three of these variables means the fourth is controlled by the correlation. The following examination of the four components discloses that a workable control of the four-component system is feasible.

It has already been shown that the nature of the asphalt is important in a paving stock, and that the nature is expressed by the viscosity gravity constant of the refined asphalt which is also predetermined by the selection of the crude stock from which the asphalt product is obtained. Thus, one variable of the four-component system is predetermined at the outset of each refining operation.

The penetration variable in the four component system is set by the specifications required for the specific asphalt being prepared. Thus, the variable of penetration value is predetermined. The penetration—or consistency—of the asphalt is, as earlier pointed out, the most commonly specified property of asphaltic materials and is governed by the use to which the asphalt is to be applied. It is a specified value which the asphalt must meet to be satisfactory for the intended use.

Since the asphalt product is a four variable system and such a system is necessarily determined by fixing three variables, the refiner may now elect to fix one of the two remaining variables. Because of the ease of operating and controlling a distillation apparatus as compared to an asphalt oxidizer, the practical election is petrole viscosity. The crude is simply reduced until the desired petrole viscosity is attained. The residuum may then be oxidized (i. e., petrolenes converted to asphaltenes) until the product has the proper penetration without appreciably changing petrole viscosity.

If the variable weight percent of asphaltenes was chosen, the refiner would first have to oxidize his soft residual crude to obtain the desired asphaltene content. Thereafter, removal of petrolenes by distillation (to reach required penetration value) would alter the per cent asphaltenes. This situation thus leads to an impractical "cut and try" method in order to make the final product.

Of the four components determining the properties of the asphalt product, therefore, only two variables, that is, the petrole viscosity or weight percent of asphaltenes are left to be varied in the preparation of asphaltic material from any given crude oil stock. For the foregoing reasons, the election is made to vary petrole viscosity.

Furthermore, it is found that the asphalt properties relating to the other important properties of bleeding tendencies, deformation at low temperatures (such as 32° F.), resistance to oxidation (weathering), resistance to stripping, ductility and softening point are directly related to the viscosity of the petrole fraction of asphalt cements. Thus, all the important properties of an asphalt product for paving purposes, are related to the three variables which define the value of "n" and determine the flow properties of an asphalt. By far the greater number of these properties are related particularly to the viscosity of the petrole fraction. Conveniently, this is the variable which is most readily controlled.

Hence, a control of the several properties of the asphalt products to be used for paving purposes may be effected by controlling the viscosity of the petrole fraction, and it is found that when petrole viscosity is controlled within certain limits in the preparation of asphaltic materials from a suitable crude oil source, that is, a crude oil of a suitable nature as defined by its viscosity gravity constant, a product is obtained which possesses the indicated desirable characteristics.

By setting a minimum and a maximum value of "n" which will satisfy the specifications for softening point, ductility and temperature susceptibility, a range of petrole viscosity which will assure satisfactory values of these properties within specified limits is also set. An operating range within which the petrole viscosity shall

be controlled can now be established from these relationships to provide asphaltic products having these desired characteristics.

However, the maximum and minimum satisfactory petrole viscosities are found to be slightly different for asphalts of varying basic nature and attention must be had as to the suitability of asphalts for paving purposes as governed by the nature of the asphalt. Thus as pointed out earlier it must not be too paraffinic nor must it be too extensively cracked, that is, contain too great a quantity of aromatics. Suitable asphaltic materials for paving purposes are found to have a viscosity gravity constant between 0.82 to 0.94. Crude petroleum and asphalt stocks will therefore of necessity be selected initially from material which will result in an asphaltic product of desirable viscosity gravity constant.

Oxidation resistance is still another important property of asphalts for paving purposes which must be considered. It is found also to be related to the viscosity of the petrole fraction of the asphalt and to the nature of the asphalt as expressed by the viscosity gravity constant.

Thus there are sufficient variables all related to the petrole viscosity of asphalts having a viscosity gravity constant between 0.82 and 0.94 to establish an operable range of control of petrole viscosity to assure a resulting asphalt of satisfactory properties of "n" and thereby of softening point, ductility and temperature susceptibility and also of oxidation resistance.

In the accompanying drawing, Figure 1 is a graph showing petrole 100° F. viscosity gravity constants plotted against petrole viscosity of 77° F. (poises). The area ABCD of the graph is the permissible operating area of this invention.

Figures 2 and 3 show the curves obtained by plotting successive values of *a* and *b*, respectively, against penetration at 77° F. (100 grams—5 seconds). The values *a* and *b* are defined below.

In Figure 1, the overall operating area is defined by the figure ABCD. The line AC is the minimum petrole viscosity which an asphaltic material may have for the asphalts of various desirable petrole viscosity gravity constant values to assure a satisfactory product for paving purposes for all asphalt products of penetrations higher than "50 penetration." This minimum is found to be slightly lower for asphalts of some penetrations higher than 50, but the minimum represented by the line AC is within the minimum for asphalts of all penetrations above 50. This minimum is determined by the permissible minimums of softening point and ductility. Maximum petrole viscosities for various product penetration values for asphalts of the various values of petrole viscosity gravity constants are defined by appropriate lines EF and are established by the permissible limits of temperature susceptibility. All suitable maximum petrole viscosities for the various product penetrations to assure suitable properties for the finished asphalt are further limited by the factor of oxidation resistance, the limits of which are represented by line BD. For suitable paving asphalts the viscosity gravity constant must not be below 0.82 represented by line CD nor above 0.94 represented by line AB. An operating area is thereby defined by the various limitations on the properties of the asphalt product.

Thus for a product asphalt of 50 penetration, the permissible values of petrole viscosities at 77° for the product asphalts whose petrole fraction has a V. G. C. between 0.82 and 0.94 is defined by the area AEFC, all of the values falling below the permissible maximum set by limitations of oxidation resistance (line BD).

Similarly for a product asphalt of 70 penetration, the permissible values of petrole viscosity at 77° for asphalts whose petrole fraction has a V. G. C between 0.82 and 0.94 is defined by the area AE'F'DC. In this instance, limitations due to undesirable oxidation properties appear in the extreme outer petrole viscosity values for those asphalts in the lower V. G. C.

regions so that it is necessary for consistently satisfactory results to restrict the outer range by the further limit defined by the line F'D (which is a part of the limiting curve BD).

Again for a product asphalt of 90 penetration, the permissible values are defined similarly by the area AE''F''DC, the outer limit of the range for asphalts of lower V. G. C. being limited by the line F''D.

Other product asphalts of other final penetration values have permissible petrolene viscosity values within a minimum established for V. G. C. stocks between 0.82 (line CD) and 0.94 (line AB) by the line AC which may be represented by the formula:

$$V=10\left(\frac{G-1.2877}{-0.1214}\right)$$

where G is the 100° V. G. C. of the petrolene and V is the 77° viscosity of the petrolene.

The maximum values are limited by oxidation properties (line BD) and an upper limit defined by a line E\*F\* which is a function of the 100° V. G. C. (G) of the petrolene and the final penetration (P) represented by the following formula:

$$V=10\left(\frac{G-a}{b}\right)$$

where V is the 77° F. viscosity of the petrolenes and where a may be represented by the formula:

$$a=1.1511-0.000318P+173850P^{-3.632}$$

and b may be represented by the formula:

$$b=-0.0114+0.000385P-2.103\times 10^{14}P^{-9.393}$$

the values of which may be read directly from Figs. 2 and 3, respectively.

It is found that the petrolene viscosity decreases but slightly during the oxidation of a crude petroleum distillative residue. Thus, it is possible to distill the crude petroleum to the point at which the residue has a petrolene viscosity within the desired range and from this residue an asphaltic product of the desired final penetration value may be obtained by oxidizing the residue until the product has the prescribed or required penetration value P. The desired petrolene viscosity to which the crude petroleum residue will be reduced will, as brought out before, be above a minimum value represented by a line AC of Figure 1 and below a maximum value limited by values on lines BD and E\*F\*, the particular line EF being governed by the prescribed final penetration value P as defined by the formula above.

The petrolene viscosity may be set in several different ways. The crude oil may be reduced directly to a point where the petrolene viscosity is in the preferred range or the crude oil may be reduced to a point where the petrolene viscosity is in excess of the maximum of the preferred range and then diluted with lighter blending stock, such as cylinder stock, to reduce the petrolene viscosity to the desired point. The petrolene viscosity may also be decreased by various other means, such as a light cracking treatment or changing the refining operations to remove less of the lighter constituents.

In conducting the present process, samples of the crude residue being refined are separated into the asphaltene fraction and the petrolene fraction is tested to determine if its viscosity is within the desired range. This is accomplished by mixing the asphalt sample with 50 volumes of n-pentane per volume of asphalt at room temperature to dissolve the petrolenes. The solution is filtered from the undissolved asphaltenes and the petrolenes are recovered from pentane solution by distilling to a small volume and then evacuating while heating on a steam bath until constant weight is attained. The viscosity of the petrolenes is then measured in absolute units, poises, using the Koppers' viscometer, proposed

by Rhodes et al., Eng. News-Record 115, p. 714 (1935). If the petrolene viscosity is not within the prescribed operating limits for an asphaltic material of the indicated viscosity gravity constant, the refining operations are adjusted to provide a residue of the desired petrolene viscosity. When the petrolene viscosity is adjusted satisfactorily, the refining is completed to the desired final penetration by oxidation of the adjusted residue.

The present method of control of the properties of asphaltic materials is particularly advantageous, inasmuch as the petrolene viscosity may be readily determined in the laboratory and thus a highly desirable plant control in the preparation of asphaltic materials is available.

The following examples are given as illustrative of the manner of refining to prepare asphaltic materials of the desired final penetration value having the other desirable characteristics in accordance with the invention. It is to be understood that these are merely illustrative of the operations which may be performed in accordance with the invention in order to obtain desired asphaltic products.

#### Example A

The residuum of a crude petroleum stock, the petrolene fraction of which had a viscosity gravity constant of 0.862, was subjected to distillation to a maximum temperature of 570° F. at 0.002 mm. The distillative residue was observed to have a final penetration value of 57, and a petrolene viscosity at 77° F. of 51,500. The temperature susceptibility value was found to be 4.61, the ductility at 77° F. was 110+ and the softening point (R & B) was 116° F. This product was found, therefore, not to meet the specifications of temperature susceptibility and softening point desired, as shown by the table.

#### Example I

Another sample of the same residuum used in Example A was distilled to a maximum temperature of 518° F. at 0.002 mm. The petrolene viscosity was observed to be 8,150 and the penetration value was 261. The distillative residue was then oxidized by blowing air through the residue at a temperature of 425-475° F. for 8.5 hours and the final penetration value was found to be 60. The temperature susceptibility of this residue was 3.37, the ductility at 77° F. was 110+ and the softening point (R & B) was 122° F.

#### Example II

A sample of asphaltic residuum obtained by propane precipitation from a crude petroleum was found to contain petrolenes of 3,600,000 poises viscosity and to have a ductility at 77° F. of 0, penetration at 77° F. of 0, and a ring and ball softening point of 225° F. This was blended with a soft distillation residuum so as to obtain a blend of 128 penetration at 77° F., and containing petrolenes of 0.895 V. G. C. and 72,100 poises viscosity. On oxidation to 77 penetration the final product had a ductility of 110+, a temperature susceptibility of 4.82, a ring and ball softening point of 109° F., and the oxidation test result was 2.61 cc. This asphalt failed to meet specification requirements for temperature susceptibility, softening point, and oxidation resistance, as shown by the table.

#### Example III

A sample of asphaltic residuum obtained by propane precipitation from a crude petroleum was found to contain petrolenes of 3,600,000 poises viscosity, and to have a ductility at 77° F. of 0, penetration at 77° F. of 0, and a ring and ball softening point of 225° F. This was blended with a soft distillation residuum so as to obtain petrolenes in the blend of 20,700 poises viscosity and 0.836 viscosity-gravity constant. The penetration of the blend was 70, the temperature susceptibility 2.80, the

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ductility at 77° F. was 110+, and the ring and ball softening point was 120° F.

This example shows, in contrast to Example II, that an asphaltic residuum obtained by propane precipitation can be employed for the manufacture of an asphalt having all the specification requirements shown in the table.

*Example IV*

A crude petroleum residuum whose petrolene fraction had a viscosity gravity constant of 0.830, was distilled to a penetration value of 98 and the petrolene viscosity was adjusted to 18,200. The residue was then oxidized as in Example I to a final penetration value of 90. The temperature susceptibility of the final product was found to be 3.75, the ductility at 77° F. was 110+ and the softening point (R & B) was 117° F.

*Example V*

A crude petroleum residuum, whose petrolene fraction had a viscosity gravity constant of 0.890 was distilled until the viscosity in the petrolene fraction was 2100 poises. The penetration was 63. The temperature susceptibility was found to be 3.10, the ductility at 77° F. was 110+ and the softening point (R & B) was 124° F.

*Example VI*

A crude petroleum residuum, the petrolene fraction of which had a viscosity gravity constant of 0.918, was distilled to a penetration value of 85. The petrolene viscosity of the residue was found to be 1750. The temperature susceptibility was 2.68, the ductility at 77° F. was 110+, and the softening point was 116° F.

*Example VII*

A crude petroleum whose petrolene fraction had a viscosity-gravity constant of 0.822 was distilled to a soft residuum containing petroleues of 1630 poises viscosity. The residuum was then oxidized by air blowing at a temperature of 425-475° F. to a final penetration of 70. The temperature susceptibility was 2.90, the ductility at 77° F. was only 36, and the ring and ball softening point was 139° F. This product did not meet the desired specifications, especially in ductility and softening point.

*Example VIII*

Another sample of the same crude petroleum used in Example VII was distilled to a residue of 300 penetration at 77° F. The petrolene viscosity of this residue was 7140 poises. This residue was then oxidized by air blowing at 425-475° F. for 12½ hours to a final penetration of 70. The temperature susceptibility was 2.69, the ductility at 77° F. was 110+, and the ring and ball softening point was 123° F. This product met the desired specifications of the table.

From the foregoing examples, I to VII, it is seen that the temperature susceptibility, ductility, and softening point properties of asphaltic products whose petrolene viscosity is within the range of values defined by the area ABCD of Fig. 1 possess satisfactory characteristics. Those asphaltic products whose petrolene viscosities are outside of the values defined by the area ABCD are not satisfactory in at least some of their properties. Thus, the specifications, in the table, of temperature susceptibility and softening point are not met by the product of Example A. All of the specifications are met by the products of Examples I, III, IV, V, VI, and VIII. The specifications of temperature susceptibility, softening point, and oxidation resistance are not met by the product of Example II. The specifications of ductility and softening point are not met by the product of Example VII.

It is seen, therefore, that by controlling the preparation of asphaltic products according to this invention where the petrolene viscosity at 77° F. is adjusted to a value within the area ABCD of Fig. 1 and further limited by a maximum limitation value which is the function of the final penetration value P, asphaltic products may be consistently produced which will possess desired proper-

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ties for paving purposes. Although it may occur that asphaltic products whose properties are slightly outside the area ABCD will be satisfactory there is not the assurance that all of the properties will be satisfactory as there is when the production of the asphalts are conducted so that the product falls within the area ABCD.

It will be understood that lines E<sup>x</sup>F<sup>x</sup> shown in Fig. 1 are merely illustrative and that there is a continuous pattern of consecutive lines falling between the lines AB and BD for various penetration values, the slope and location of which are peculiar to the respective penetration values.

I claim:

1. A method of preparing improved asphaltic material for paving purposes having a final penetration value of P, which comprises reducing a petroleum crude oil, the petrolene fraction of the residue of which has a viscosity gravity constant (V. G. C.) between 0.82 and 0.94, to produce a residuum having a predetermined penetration different from said final penetration; separating a sample of the reduced residuum into asphaltenes and petroleues; determining the viscosity of the separated petroleues; altering the viscosity of the petroleues of the residuum, if necessary, to a value within the range defined by the area ABCD of Fig. 1 for said V. G. C. value and below a value represented by a curve EF which is defined as a function of the final penetration P by the following relation:

$$V=10\left(\frac{G-a}{b}\right)$$

where V is the 77° F. viscosity of the petroleues, where G is the 100° V. G. C. of the petrolene fraction and a is represented by the formula

$$(a=1.1511-0.000318P+173850P^{-3.632})$$

and the curve of Fig. 2 and b is represented by the formula

$$(b=0.0114+0.000385P-2.103 \times 10^{14}P^{-9.393})$$

and the curve of Fig. 3; and altering the penetration of the residuum to said final penetration value P.

2. A method of preparing improved asphaltic material for paving purposes having a final penetration value of P, which comprises reducing a petroleum crude oil, the petrolene fraction of the residue of which has a viscosity gravity constant (V. G. C.) between 0.82 and 0.94, to produce a residuum having a predetermined penetration in excess of the final desired penetration; separating a sample of the reduced residuum into asphaltenes and petroleues; determining the viscosity of the separated petroleues; altering the viscosity of the petroleues of the residuum, if necessary, to a value within the range defined by the area of ABCD of Fig. 1 for said V. G. C. value and below a value represented by a curve EF which is defined as a function of the final penetration P by the following relation:

$$V=10\left(\frac{G-a}{b}\right)$$

where V is the 77° F. viscosity of the petroleues, where G is the 100° V. G. C. of the petrolene fraction and a is represented by the formula

$$(a=1.1511-0.000318P+173850P^{-3.632})$$

and the curve of Fig. 2 and b is represented by the formula

$$(b=0.0114+0.000385P-2.103 \times 10^{14}P^{-9.393})$$

and the curve of Fig. 3; and then oxidizing the residuum to said final penetration value P.

References Cited in the file of this patent

UNITED STATES PATENTS

2,276,155 Carr ----- Mar. 10, 1942