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PROCESS FOR THE PREPARATION OF AGE RESISTANT ASPHALT COMPOSITIONS

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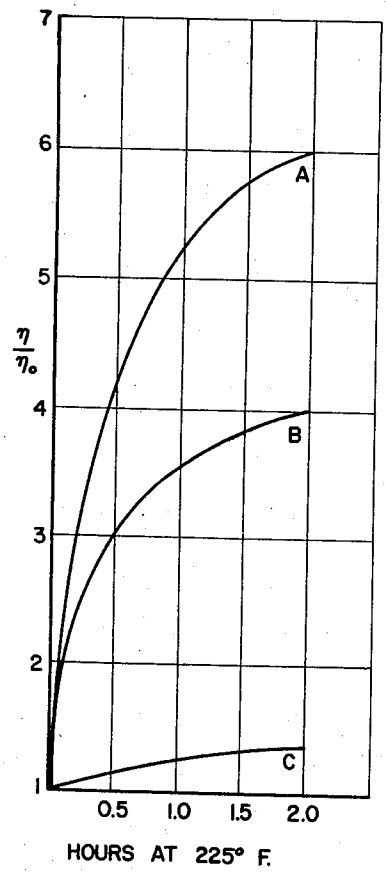


FIG I

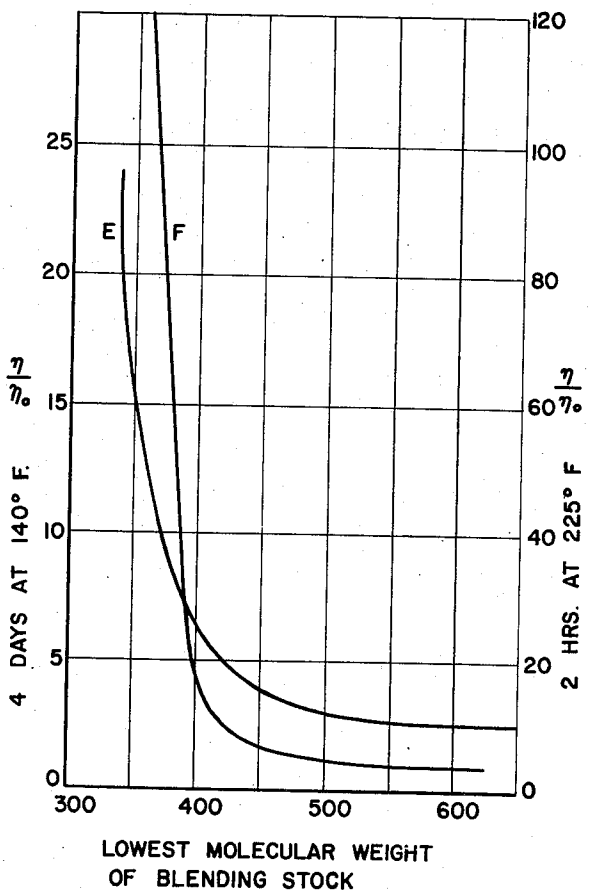


FIG II

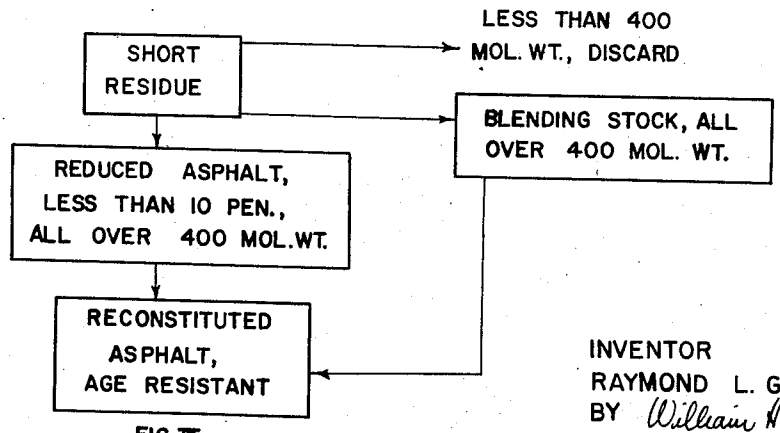


FIG III

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PROCESS FOR THE PREPARATION OF AGE RESISTANT ASPHALT COMPOSITIONS

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5 Claims. (Cl. 208—23)

This invention relates to a process for the improvement of asphalt compositions. More particularly, it relates to a process for improving the aging characteristics of asphalts.

Asphalts normally comprise straight run asphalts, cracked asphalts, and blown asphalts prepared from either of these materials, either with or without the aid of oxidation catalysts. The term "asphalt" is generally directed to residues obtained from the distillation of petroleum and may vary from extremely soft materials to hard, brittle compositions exhibiting a conchoidal fracture. They are used principally in the preparation of pavings of various kinds, as well as in roofing materials, pipe coatings, enamels, and the like.

In many instances it is desirable to utilize products which remain stable insofar as their viscosity or consistency is concerned during the life of the product. For example, in road compositions it is highly desirable to maintain the same consistency of pavement commensurate with changes in temperature encountered during its life. However, this ideal state is seldom if ever reached and many explanations for changes in the properties of asphalt during its life or use have been advanced. These changes have been attributed to oxidation, changes in gel structure with aging, sources of the asphalt, components naturally present in a given petroleum crude, temperature of application insofar as it affects the structure of the components, mechanical stress and vibration to which the composition is subjected, and numerous other influences.

It is a well-known fact that these changes in physical properties seriously limit the use of asphalts for many purposes and also greatly shorten the useful life of asphalts for such purposes as roofing or more particularly, in pavements such as roads, etc. The problem of aging is especially evidenced by a hardening of the asphalt. The increase in consistency, i.e. viscosity, of the asphalt leads to secondary undesirable effects such as cracking or stiffening of the article with which or in which the asphalt is incorporated. In roads, for example, this can lead to disintegration of the road as the asphalt becomes harder and is subjected to the vibration and stress caused by traffic. The problem becomes accentuated in the asphalts having relatively low penetrations and high viscosities. Likewise, the undesirable increase in viscosity is noted especially where the asphalt is subjected either to high temperatures, or to oxidation influences, as well as to combinations of these environments. Thus, it will be seen that asphalts normally employed either for paving or roofing purposes are especially subject to this undesirable process of age hardening.

It is an object of the present invention to improve the aging properties of asphalt compositions. It is another object of this invention to produce asphalts showing relatively high stability with respect to viscosity change during its useful life. It is a particular object of this

invention to improve the aging characteristics of asphalts heretofore regarded as being unstable with respect to aging. Other objects will become apparent from the description of the invention.

Now, in accordance with the present invention, it has been found that the aging stability of asphalts may be strikingly improved, especially in asphalts containing more than about 5% by weight of components having molecular weights of less than 400, by reduction of such asphalts to asphaltic residues having penetrations of less than about 10 and thereafter mixing with said asphalt an asphaltic cutter stock in an amount sufficient to provide an asphalt composition of a desired penetration grade, said cutter stock containing substantially no components having molecular weights less than about 400. The invention may be described in similar terms by stating that the asphaltic residue should be reduced such as by distillation so as to contain no components having molecular weights less than about 400 and thereafter blending the reduced residue with the cutter stock defined hereinbefore.

In the description hereinafter, certain terms are to be understood as follows: Asphalt is regarded as the residue obtained by the elimination of relatively lower boiling components of petroleum to obtain a composition composed of comparatively non-volatile components, principally hydrocarbons, and substantially free from oxygenated bodies with little or no crystallizable paraffins. The scope of the definition given on page 56 of the Fourth Edition of Abraham "Asphalts and Allied Substances" is regarded as the definition to be accepted here.

The term "cutter stock" is understood for the present purpose to mean relatively non-volatile components, preferably derived by the distillation of short residues and other residual oils. The cutter stocks so utilized are to be defined as having substantially no components of molecular weight below about 400, and preferably substantially no components having molecular weights lower than about 450. The upper limit of the molecular weight of components present in the cutter stock is immaterial to the practice of the present invention, since the critical limitation placed upon the present invention is with respect to the lowest permissible molecular weight components. The cutter stock, therefore, may comprise even a whole asphalt as long as the composition contains substantially no components having molecular weights less than about 400. Normally, however, the cutter stocks will comprise components falling within the boiling point range of those which will first distill, such as in vacuum, from a petroleum residue immediately following the elimination of those having molecular weights below about 400, that is, those having molecular weights between about 400 and about 800. Their preparation will be described more fully hereinafter.

The term "penetration" will be understood to refer to the consistency or hardness of semi-solid and solid asphalts as determined by the ASTM Method D5–25. The penetration is expressed in terms of hundredths of a centimeter which a standard needle penetrates a sample of asphalt under standard conditions of load, time and temperature. Unless otherwise specified, the penetration as discussed in the present specification is that determined at 25° C. (77° F.) with a 100 gram load and 5 seconds time.

Wherever reference is made to viscosity throughout the specification (unless otherwise specified) it will be understood that the viscosity is given in poises and that the determination was made by the micro method described in a paper presented before the Division of Petroleum Chemistry of the American Chemical Society

at their New York meeting September 11–17, 1954, by Labout and Van Oort. In this method, samples in the order of 12–30 milligrams are aged on glass plates in films only a few microns thick under prescribed conditions. The viscosity of the aged material is then determined by means of a microviscometer, also described in the paper referred to. Of course, samples may be tested in the microviscometer without previously having been aged.

Asphalts falling within the above definition of asphalts generally, include those derived from a straight distillation operation and normally referred to as "steam refined asphalts" as well as "cracked asphalts." The present invention is especially applicable to cracked asphalts, since these are notorious for their poor aging characteristics when utilized as known heretofore. However, the process applies both to cracked asphalts and to straight run asphalts, as well as to blown products prepared from asphalts derived by either process. The blown asphalts are regarded as asphalts which have been subjected to an oxidation process usually involving oxygen and, more normally, air at relatively elevated temperatures for a time sufficient to decrease the penetration of the product and make it more suitable for such purposes as used in roofing compositions, and the like. The oxidation or blowing may take place without any modification but may be conducted in the presence of such catalysts as ferric chloride, phosphoric acid, phosphorus pentoxide, aluminum chloride, chlorine, Friedel-Crafts catalysts, and other well-known blowing catalysts.

The invention will be described with reference, in part, to the accompanying drawing, wherein:

Fig. I shows the aging stability as measured by change in viscosity of several asphalts containing blending stocks having minimum molecular weights below 400 and above 400, respectively;

Fig. II shows the effect of varying molecular weights upon the aging stability of a Santa Maria asphalt at two different aging temperatures; and

Fig. III is a schematic representation of a typical process illustrative of the invention.

A surprising feature of the present invention is the entirely unexpected difference between the effect of blending stocks containing components of less than 400 molecular weight as compared to the aging effect of blending stocks having components above 400 molecular weight minimum. This is clearly illustrated by the examples and the results shown in the drawing. The precise reason for this striking difference in behavior has not been clearly ascertained. However, as Fig. II illustrates, it is not merely a direct correlation between molecular weight and the temperature of aging. The sharp difference between blending stocks having minimum molecular weight components above and below 400 molecular weight, respectively, is as evident at a test temperature of 140° F. as it is at a test temperature of 225° F. Since the blending stocks were derived by molecular distillation or vacuum distillation of short residues, it would be expected that the individual components would be similar in structure and merely gradually change in molecular weight as the boiling point of the blending stock is elevated. Even if this is true, however, then it merely emphasizes the surprising feature referred to and illustrated so clearly in the drawing which shows the sharp rise in the rate of aging when blending stock components have molecular weights below 400.

The blending stocks are employed in amounts sufficient to render the reduced asphalt suitable for use as paving grade asphalts, coating grade asphalts, roofing asphalts, and the like. The reduced asphalts are meant to be the asphalts referred to hereinbefore, obtainable, for example, from short residues or long residues from which the lower boiling components had been removed

to an extent that the reduced asphaltic residue has a penetration of less than about 10 and contains substantially no components of less than 400 molecular weight.

In blending such residues back to a penetration suitable for paving grade asphalt, it is normally found that between about 50% and about 90% of the blending stock is required. For roofing grade asphalts, it is normally necessary to utilize between about 40% and about 70% by weight of the final composition of the subject blending stocks. Paving grade asphalts normally have penetrations between about 40 and about 250 at 77° F. and softening points between about 100° and 130° F. as measured by the ASTM ring and ball method. Roofing grade asphalts, on the other hand, normally have penetrations of between about 11 and 40 at 77° F. and softening points between about 140° and 220° F. Paving grade asphalts have high ductilities, usually above about 100 at 77° F. as measured by the ASTM method, while roofing grade asphalts have low ductilities in the order of 1–5 centimeters minimum at 77° F.

In carrying out the process of the present invention, the hard asphalts, referred to hereinbefore as reduced asphalts, may be prepared by any number of well-known methods as long as substantially all of the components present having molecular weights less than about 400 are removed. This can be done by steam refining or vacuum distillation of short or long residues, care being taken toward the end of the reduction process that all of the lower molecular weight components, i.e. below 400 molecular weight, are removed. Combinations of cracking and vacuum distillation occurring either simultaneously or in steps subsequent to one another may be employed, either with or without steam distillation. In the use of vacuum distillation, it is normally found that temperatures in the order of at least about 200° C. are necessary to remove substantially all of the components having molecular weights below about 400 when the vacuum employed is between about 1.0 and about 2.0 mm. Hg pressure, absolute.

When employing thermal cracking conditions, it is usually preferred to subject the residue to cracking initially while removing the relatively volatile products so produced and thereafter subjecting the remaining residue to a vacuum distillation for the further removal of moderately volatile materials. The latter are then re-fractionated for the removal of components having molecular weights of less than about 400, after which at least part of the residue from the refractionation (having components substantially all of which are of more than 400 molecular weight) is reblended with the reduced residue for the preparation of paving or coating grade asphalts of improved aging stability.

As will be seen by examination of the Figs. I and II, the incorporation of blending stocks containing components of less than about 400 molecular weight results in asphalt compositions which age at a far greater rate than those wherein the components of less than 400 molecular weight are absent. The rate of viscosity change upon aging breaks sharply at just about 400 molecular weight, regardless of the source of the blending stock and regardless of the specific hard asphalt with which the blending stock is used. Consequently, one aspect of the present invention comprises cross-blending, by which is meant the utilization of blending stocks containing components of over 400 molecular weight only combined as described hereinbefore with hard asphalts of the same or of different origins, i.e. from the same or different crudes, so that advantage may be taken not only of the high aging stability characteristics due to the selected blending stock molecular weight components, but also to the secondary advantages relative to the proportion and molecular configuration of the aromatics, saturates and resins present in both the blending stocks and in the reduced asphalts combined therewith.

As pointed out hereinbefore, Fig. I illustrates the rate of aging of asphalt compositions, some of which contain blending components of less than 400 molecular weight, and others of which contain components of greater than 400 molecular weight minimum. Curve A illustrates the aging rate of a cracked asphalt containing blending components having a minimum of 370 molecular weight. This cracked asphalt was derived from a Gulf-Stettler crude subjected to an initial thermal cracking operation, followed by a vacuum distillation. In the course of the latter operation the residue was reduced to an asphalt having zero penetration and containing no components of less than 400 molecular weight. Thereafter, 45% by weight of a blending stock having components of 370 molecular weight minimum was combined with the hard residue to obtain an asphalt having a penetration of 84 and an initial viscosity of 1.80×10^6 poises, as measured by the microviscometer referred to hereinbefore, the viscosity being measured at 25° C. According to the data given in Fig. I, it will be seen that this blend when aged in air at 225° F. had 4½ times its original viscosity after 0.5 hour.

Curve C in Fig. I represents another composition based on the same reduced asphalt derived from Gulf-Stettler crude by the same cracking process. However, the minimum molecular weight of the blending stock combined therewith was 427. An insignificant viscosity increase occurred when this particular blend was aged in air at 225° F. for 2 hours. This same curve also represents a third blend wherein the reduced asphalt was the same as that employed in the previous two samples but wherein the blending stock contained components of a minimum of 515 molecular weight. This blend also showed a remarkable resistance to viscosity increase upon aging.

Curve B in Fig. I illustrates a second cracked asphalt composition, in this case derived from Alberta Crude. As in the case of the Gulf-Stettler samples, the Alberta short residue was subjected to a cracking operation followed by a vacuum distillation to obtain a reduced asphalt residue having zero penetration of 77° F. This was blended with components removed during the vacuum distillation, the minimum molecular weight of said components being 322. Curve B shows that this blend tripled in viscosity after aging for 0.5 hour in air at 225° F. This blend contained 59% by weight of the blending stock and the latter comprised components boiling between about 420° C. at 760 mm. and about 455° C.+ at 760 mm. and having molecular weights between about 322 and about 496. Seven percent of the composition had a molecular weight of about 322.

When this same reduced asphalt from Alberta crude was blended with blending stock components having a minimum molecular weight of 496, 63% by weight of the blending stock being employed, and the latter containing components boiling above 455° C. at 760 mm., the resulting asphalt composition was extremely stable, as shown by the substantial lack of viscosity change indicated by Curve C in Fig. I.

Fig. II represents the aging characteristics of a Santa Maria reduced straight run asphalt combined with blending stocks of a variety of minimum molecular weights, these blends being tested at two temperatures. Curve E represents the results obtained by blending the asphalt (having a penetration of about 0–10 and containing no components of less than 400 molecular weight) with blending stock components obtained by the molecular distillation of Santa Maria short residue to obtain a blended composition of 85–100 penetration at 77° F. These blends contained the following proportions of the specific blending stocks listed as follows:

Lowest molecular weight:	Percent in blend
350	50
400	58
510	66

Molecular weight distribution, Santa Maria blends

Blend	1 354+ M.W.	2 400+ M.W.	3 510+ M.W.
	Percent weight in blend		
Mol. Wt.: Cutter stock—			
354	8.80		
360	8.90		
393	8.65	15.54	
508	8.70	15.60	24.29
613	9.35	16.82	26.14
778	5.60	10.04	15.57
Molecular distillation, bottoms	50.0	42.0	34.0

Curve F of Fig. II shows that the blend containing components of 350 molecular weight minimum aged extremely rapidly when the compositions were heated in air for 2 hours at 225° F. However, the remaining two blends containing 400 and 510 minimum molecular weight blending components, respectively, showed substantially no change in viscosity under these test conditions.

Curve E in Fig. II represents the same blends, as well as some intermediate blends heated for four days at 140° F. in air. The change in viscosity, while of lesser order, is just as striking as in the case of samples heated at the higher temperatures. Blends containing components of less than about 400 molecular weight aged extremely rapidly, the viscosity of the aged blends reaching up to 23 times that of the original sample, as compared with 2–3 times viscosity increase for samples wherein the blending components were greater than a minimum of 400 molecular weight.

Fig. III represents a typical process by which the subject age-resistant asphalt compositions may be prepared. In the process as represented, short residue is subjected to a distillation process. It will be understood that this may be accompanied or preceded by previous treatments such as cracking and/or vacuum flashing. The distillation may be at atmospheric pressure or reduced pressure. Preferably the distillation is arranged so that cuts may be taken, thus separating as desired those of lower boiling point and lower molecular weight from those of relatively higher molecular weight. Preferably the separation is such that those having molecular weights above 400 minimum are segregated from the components containing molecules of less than 400 molecular weight each. When the reduced asphalt so obtained has a penetration of less than about 10 and contains substantially no components of less than 400 molecular weight, it is considered that the base stock, i.e. the reduced asphalt, is in proper condition for blending. For this blending purpose, at least a portion of the distillation cuts having minimum molecular weights of at least about 400 are blended with the reduced asphalt so as to reconstitute an asphalt composition having paving, coating or roofing characteristics. It will be understood, as brought out hereinbefore, that the blending stocks having molecular weights above about 400 minimum may be derived from other sources than the asphalt from which the reduced asphalt base is prepared.

I claim as my invention:

1. In the process of preparing asphalts having improved aging stability, the steps comprising distilling a petroleum residue containing more than about 5% by weight of fractions of less than 400 molecular weight until the distillation products finally contain no components of less than 400 molecular weight, whereby a reduced residue having improved stability is formed, said reduced residue having a penetration less than about 10 at 77° F., and thereafter blending therewith 40–90% based on the blended composition of an asphaltic oil composed substantially ex-

clusively of components having molecular weights between about 400 and about 800.

2. In the process of preparing asphalts having improved aging stability, the steps comprising distilling a petroleum residue containing more than about 5% by weight of fractions of less than 400 molecular weight until the distillation products finally contain no components of less than 400 molecular weight, whereby a reduced residue having improved aging stability is formed, said reduced residue having a penetration less than about 10 at 77° F., and thereafter adding to said residue a cutter stock, substantially all the components of which have molecular weights greater than about 400 in an amount sufficient to form an asphalt composition having paving grade characteristics.

3. In the process of preparing asphalts having improved aging stability, the steps comprising distilling a petroleum residue containing more than about 5% by weight of fractions of less than 400 molecular weight until the distillation products finally contain no components of less than 400 molecular weight, whereby a reduced residue having improved stability is formed, said reduced residue having a penetration less than about 10 minimum at 77° F., and thereafter adding to said residue a cutter stock substantially all the components of which have molecular weights greater than about 400 in an amount sufficient to form an asphalt composition having roofing grade characteristics.

4. In the process of preparing asphalts having improved aging stability, the steps comprising first distilling a petroleum residue containing more than about 5% by weight of fractions of less than 400 molecular weight until the reduced residue so formed finally contains no components of less than 400 molecular weight, volatilizing from the distillate obtained in said first step substantially

all of the components having molecular weights below about 400, leaving a residual cutter stock composed essentially only of components having molecular weights above about 400, and recycling at least a portion of said cutter stock to the reduced residue.

5. An asphalt composition comprising a residual asphalt having a penetration at 77° F. less than 10 and a cutter stock comprising petroleum hydrocarbons in an amount between about 40 and 90%, said cutter stock being an asphaltic oil having molecular weights between about 400 and 800, said asphalt composition containing substantially no components having molecular weights less than about 400.

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