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ASPHALTIC PRODUCTS

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This invention relates as indicated to improved asphaltic products. More particularly it relates to a process for the preparation of asphaltic materials by a novel method whereby the penetration value of a petroleum residuum is reduced.

In the ordinary methods of refining petroleum a large fraction is obtained as the residue from distillation of certain crude oils. This fraction generally is referred to as the residuum, or as it has also come to be known, an asphalt flux. This latter terminology indicates the principal effectiveness of this fraction as a starting material in the preparation of asphalt. This petroleum residuum or asphalt flux is a dark, very viscous fluid. It is susceptible to further distillation, but ordinarily the distillation of the crude oil is halted while some "volatile" material yet remains so as to minimize the thermal decomposition of this residue. Further distillation of this residue, while resulting in appreciable decomposition, results also in the formation of a type of asphalt and except for the above noted thermal decomposition, asphalt could well be produced simply by a continuation of the distillation. The decomposition results not only in the loss of a substantial proportion of material, but also in the formation of large quantities of coke, and the presence of such coke in the product is a serious disadvantage with respect to its use as an asphaltic material.

The principal production of asphalt, therefore, depends upon interrupting this distillation before the onset of substantial decomposition of the residuum and then treating this residuum, or asphalt flux, with steam and/or air. Such treatment minimizes losses by decomposition and results in a very satisfactory asphaltic product. The steam treatment is a steam distillation which allows the further removal of volatile components at a reduced temperature. The step of treating with air generally follows this steam distillation and consists merely in blowing air through the residuum at about 400° F.

The most significant change which is effected by the above processes, viz., steam distillation and air treatment, as well as by the process of this invention, is a significant reduction in the penetration value of the material. This "penetration value" measures the consistency of bituminous material, expressed as the distance that a standard needle penetrates vertically into a sample of the material under known conditions of loading, time, and temperature. These conditions are 100 grams, 5 seconds, and 25° C. (77° F.) respectively, and the units of penetration are expressed in hundredths of a centimeter. This penetration value is determined according to the procedure of ASTM test D5-52, "Standard Method of Test for Penetration of Bituminous Materials."

Another effect produced by the process of this invention is an increase in the resistance of the material to abrasion. This property is measured in terms of the weight loss of a "patty" weighing about 90 grams, comprising 98% sand and 2% of the asphalt sample, when that patty is subjected to the abrasive action of 500 grams of falling steel shot. The test is carried out by allowing the steel shot (10-14 mesh) to fall from a height of one meter onto the sand-asphalt patty as it is rotated at 360 r.p.m. The loss in weight of the patty as a consequence of this abrasive action is an indication of the resistance of the asphalt sample to abrasion. The weight loss gen-

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erally is expressed in terms of grams per 1000 grams of steel shot.

The asphaltic product which results from the process of this invention is characterized also by an improved "compressive strength," i.e., it can withstand mechanical pressure. This property is measured by subjecting a 2" x 2" cylindrically shaped sand-asphalt mixture to a weight load applied to the curved peripheral surface normal to the axis of the sand-asphalt sample. The sample is prepared by mixing 100 parts of sand with 6 parts of asphalt and forming the mixture into the shape of a cylinder 2 inches long and 2 inches in diameter. The load applied is increased gradually until the cylindrical sample will support no further load. The "load" is expressed in pounds.

The step of treating a petroleum residuum with steam and air appears to be effective as indicated above because it produces a chemical change in the petroleum residuum. This change appears furthermore to be oxidative, and this affords a logical explanation of the physical transformations which are noted. As noted before one important advantage inherent in this method of preparing asphalt is the reduced temperature of the distillation which in turn minimizes loss by decomposition. There is, however, a lesser, though still significant loss which results from the steam distillation and oxidation reaction. As the steam and air are blown through the residuum, a significant volume of material is lost by entrainment with the escaping gases.

It is accordingly a principal purpose of this invention to provide a process for the preparation of improved asphaltic products.

Another object of the present invention is the provision of an improved process for the production of asphaltic compositions.

Still another object of the present invention is the provision of a process for the production of asphaltic compositions in better yields than have heretofore been noted.

Other objects will be apparent from the following description thereof.

These objects are accomplished by the process of reducing the penetration value of a petroleum residuum to produce an improved asphaltic material which comprises preparing a mixture of 100 parts of said petroleum residuum, from about 3.5 to about 7.5 parts of a lower olefin polymer and from about 1.5 to about 3.0 parts of sulfur monochloride and heating said mixture to a temperature within the range of from about 25° C. to about 200° C. The product which results from this process is characterized by a reduced penetration value as measured by the ASTM test D-52 and by an improved resistance to abrasion and by an increased compressive strength. These latter properties are especially important with respect to the use of asphalt in the preparation of road surfaces. It is apparent that the use of asphalt for such purposes requires an extreme resistance to abrasion as well as a high order of resistance to direct pressure.

The chemical nature of the petroleum residuum employed in the process may vary considerably depending upon the particular crude oil used, especially upon the geographic origin of the crude oil used. Thus some crude stocks will yield much larger proportions of residuum than others, and the variation in chemical composition of such residua likewise is considerable. The chemical identity of these residua, however, is not important with respect to the success of the process of this invention and it is unnecessary to become concerned about the differences in such chemical identities. These residua are best defined in terms of their penetration values and as a practical matter they are characterized invariably by a penetration value within the range of from about 180 to about 250. Such limits define the range of availability of petroleum residua for use in this process.

The lower olefin polymer used in the process may be of any molecular weight above about 1,000. The higher molecular weight polymers appear to be especially effective in achieving the stated objects of the invention, i.e., the use of very high molecular weight polymer is effective to reduce the penetration value of a petroleum residuum to a greater extent than can be accomplished by the use of a lower molecular weight polymer. The same relationship appears to exist between the molecular weight of the polymeric olefin and its influence upon the change in resistance to abrasion of the residuum. An especially effective molecular weight appears to be about 50,000.

The identity of the olefin polymer reactant includes preferably the various polymers of isobutylene. Polymers of other low molecular weight olefins likewise are effective and these include ethylene, propylene, and amylene. Copolymers are useful, particularly those copolymers of the above named olefins in which these olefins are present in a predominant proportion. Specific examples of such useful copolymers are a 95-5 copolymer of isobutylene and styrene, a 98-2 copolymer of isobutylene and p-chlorostyrene, a 96-4 copolymer of isobutylene and butadiene, a 94-6 copolymer of isobutylene and isoprene, and others. The preferred polymers are the homopolymers of isobutylene. Such preference is based not only on the economic availability of these polymers, but also on their particular efficacy. The high molecular weight polyisobutylenes have been found to be most useful in the process. Thus, polyisobutylene having a molecular weight of 40,000, 50,000, and 52,000 have given good results, i.e., the asphaltic products which result from their use in the process are very much improved in all of the above mentioned properties.

The proportions of the three reactants in this process, viz., the residuum, the olefin polymer, and sulfur monochloride are critical. That is, the use of amounts of these reactants outside the stated ranges results in an asphaltic product of inferior properties. The optimum ratio of reactants appears to be about 100:5:2 respectively. The use of more residuum results in a product which is not much different from the starting residuum whereas the use of less than 100 parts of residuum results in a hard, brittle coke-like material. This latter material is of little or no value with respect to the applications of asphalt.

Ordinarily the process is carried out by mixing the residuum and olefin polymer, heating this mixture to effect an intimate mixture of the two reactants, allowing the mixed reactants to cool to about 100° C. and then adding the sulfur monochloride portionwise. The resulting reaction is exothermic so that the reaction proceeds as fast as the sulfur monochloride is added, provided that the reactants are mixed well. The process is illustrated by the following example.

A mixture of 960 grams of an asphalt flux having a penetration of 250 and 48 grams of a polyisobutylene having an average molecular weight of 50,000 was prepared and heated with stirring to 210° C. When this temperature was reached the mixture was allowed to cool to 100° C. whereupon 19.2 grams of sulfur monochloride was added portionwise, each portion being added only when the preceding portion had been consumed by the exothermic reaction. The total addition required about 10 minutes. The product mixture was heated to 225° C. and then allowed to cool. The product had a penetration value of 87, a compressive weight of 21 lbs., an abrasion value of 18.6 and an absence of "surface skin" when subjected to the thin film test. This latter (thin film) test consists in heating a thin film of the sample at 325° F. for five hours. The sample is prepared by placing 50 grams in a flat bottom aluminum dish having a diameter of 5½ inches. At the conclusion of the heating period the presence or absence of a "skin" on the surface is noted. The absence of such skin is an indication of the thermal stability of the sample.

The asphaltic products which may be prepared by the

process of this invention, as illustrated above, may be used for all known applications of asphalt. Their principal utility, of course, resides in the preparation of road surfaces. Another well known application is in the construction of built-up roof surfaces.

A particular advantage of the process of this invention is the fact that a larger yield of asphalt can be obtained from a given amount of asphalt flux or petroleum residuum, than is available from the combination of steam distillation and air blowing. As indicated earlier a significant loss of material characterizes these latter steps; there is no loss whatsoever in carrying out the process of this invention. The reason for this is the low temperature at which the process is carried out.

Still another advantage which characterizes the process described herein is the lasting quality of the product's resistance to abrasion. This property is measured by placing the asphalt-sand test patty in an infra-red oven at 140° F. for periods of time ranging up to 900 hours and then subjecting the test patty to the abrasive action of falling steel shot as described earlier herein. Such infra-red treatment deteriorates markedly the abrasive strength of asphalts prepared by previously known methods, but it appears to have only a slight effect on the products prepared by the process of this invention.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such be employed.

We therefore particularly point out and distinctly claim as our invention:

1. The process of reducing the penetration value of a petroleum residuum to produce an improved asphaltic material which comprises preparing a mixture of 100 parts of said petroleum residuum, from about 3.5 to about 7.5 parts of a lower olefin polymer having an average molecular weight above about 1,000 and from about 1.5 to about 3.0 parts of sulfur monochloride and heating said mixture to a temperature within the range of from about 25° C. to about 200° C.

2. The process of claim 1 characterized further in that the petroleum residuum has a penetration value greater than 180.

3. The process of claim 1 characterized further in that the lower olefin polymer is a polymer of isobutylene.

4. The process of claim 1 characterized further in that the lower olefin polymer is a polyisobutylene.

5. The process of claim 1 characterized further in that the lower olefin polymer is a polyisobutylene having an average molecular weight of about 50,000.

6. The process of reducing the penetration value of a petroleum residuum to produce an improved asphaltic material which comprises preparing a mixture of 100 parts of said petroleum residuum having a penetration value of at least 180, from 3.5 to about 7.5 parts of polyisobutylene having an average molecular weight above about 1,000 and from about 1.5 to about 3.0 parts of sulfur monochloride and heating said mixture to a temperature of about 100° C.

7. The process of claim 6 characterized further in that the polyisobutylene has a molecular weight of about 50,000.

8. The process of claim 6 characterized further in that the sulfur monochloride is added to a mixture of the petroleum residuum and the polyisobutylene.

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