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PRODUCTION OF BLOWN ASPHALTS

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The present invention relates to an improved method of oxidizing certain high boiling hydrocarbon fractions to produce ductile, homogeneous asphalts of high solubility in carbon tetrachloride and low temperature susceptibility. In particular, the invention relates to an improved catalytic oxidation process, employing phosphorus compounds, e.g. P_2O_5, as catalysts for the transformation of high boiling petroleum residuums and the like to asphaltic products.

The production of so-called "blown asphalts" by the air oxidation of various residual oils derived from petroleum is a well-known technique. Such "blown" asphalts are generally preferred for such purposes as coating irrigation canals, waterproofing conduits, roofing, etc. Many techniques have been proposed for the air oxidation of petroleum residuums and one of the better processes embodies the use of a phosphorus catalyst such as P_2O_5. A process of this type is described and claimed in U.S. 2,450,756 to Hoiberg. In that patent, a petroleum residuum is heated to a temperature in the range of from about 200° to about 350° F. and a small portion of that residuum is separately mixed with P_2O_5 to form a catalyst slurry. The slurry is then introduced to the main body of the residuum and the total mix is heated to a temperature in the range of from about 400° to about 550° F. while vigorously agitating and introducing large quantities of air. Asphalts produced by this blowing technique have, generally speaking, excellent properties; but it has been found that certain requirements laid down by purchasers of such materials cannot be met consistently when applying this technique to the diverse types of residual oils which are available at refineries in different parts of the country. It has been found, however, that certain modifications in the process of the aforementioned patent result in unexpected improvements in the properties of blown asphalts so prepared, almost without regard to the source of high boiling hydrocarbon charge stock.

In accordance with the present invention, a suitable residual oil, of the type hereinafter described in detail, is heated to a temperature of at least about 440° F. and preferably from about 460° to about 500° F. While this residual oil is being heated to such temperature, a relatively smaller amount, of preferably the same residual oil, is admixed with a stable phosphorus containing catalyst at a temperature in the range of from about 250 to 350° F. The catalyst slurry thus produced is rendered smooth and homogeneous by vigorous agitation at such temperature. The time required for such homogenization will vary, of course, depending upon quantities of oil, type of oil, method of agitation, etc., but for most purposes at least about ten minutes of mixing should be had and preferably from about 20 to 60 minutes. When the catalyst slurry is smooth and the main body of residual oil has been raised to a temperature of at least about 460°, the catalyst slurry is then slowly introduced to the residual oil. The slurry is added over a period of at least about one hour and preferably from about one hour and one-half to two hours while constantialy introducing large quantities of air. In accordance with the preferred embodiment of the present invention, the introduction of air is begun prior to the addition of the catalyst slurry. Thus, for example, it is highly desirable to agitate the residual oil, while maintaining the same at a temperature of about 460° F., with the air for a period of at least about 15 minutes to half an hour prior to introducing the catalyst slurry.

One of the most difficult requirements to meet in the specifications of many blown asphalt purchasers is that of asphalt should have a solubility in carbon tetrachloride of at least 97%. Prior to the discovery of the present oxidation process, it has been very difficult to consistently produce asphalts having a high solubility. As a result of the present process, however, solubilities in excess of 99% are readily and consistently obtainable and from a variety of base oils. A typical specification for blown asphalt is that of the U.S. Bureau of Reclamation for "Catalytically Blown Asphalt Cement for Buried Asphalt Canal Lining" (ASTM D–165–42). The requirement of at least 97% solubility in CCl_4 is a part thereof.

Whereas, P_2O_5 is the preferred phosphorus-containing catalyst for use in accordance herewith, it should be understood that other stable phosphorus-containing materials may be used, e.g. red phosphorus or the stable sulfides of phosphorus, such as phosphorus pentasulfide, phosphorus sesquisulfide, phosphorus sulfide, etc.

It has been found that unless each of the above mentioned features of the present process are carefully followed, a consistent production of high grade asphalt cannot be attained. Thus, for example, it is essential that the main body of residual oil be brought to oxidation temperature, i.e. about 460° F. prior to adding any catalyst and that the addition of the catalyst slurry take place over a rather extended period of time. Thus, in accordance with the preferred method of introducing the catalyst slurry, the same is sprayed by means of a suitable spray nozzle over as large a surface of the very hot residual oil as possible so that rapid and complete contact of catalyst and oil can be obtained substantially at once throughout a large volume of the oil. While not absolutely essential, it is highly desirable and in accordance with the preferred method of operation, that the catalyst slurry be heated to the temperature above indicated, viz. between about 250 and 350° F. during the formation thereof. A rather high introduction temperature is indicated in any event because of the need for a fluid, sprayable slurry. This feature, while very important, can be varied to some extent without unduly affecting the results of the process. The critical features of having the oil at oxidation temperature prior to slurry addition and slow catalyst slurry addition cannot be varied beyond the narrow limits stated.

The customary residual oil employed in the production of blown asphalts for use in the present process is a crude oil residue derived from an asphaltic or semi-asphaltic base stock. Some so-called paraffinic base stocks of the non-asphaltic base class may be blown in air in accordance with the present invention to produce highly useful asphalts, however. It is preferred to employ heavy hydrocarbon fractions derived from such petroleums as those occurring in the U.S. Gulf Coast field, the so-called Mid-Continent crude residual oil and various other asphaltic petroleums. Consistent production of satisfactory blown asphalts has heretofore been unobtainable from residual oils derived from certain sour crudes of the type found in Wyoming. However, such oils have been readily oxidized to useful asphalts in accordance herewith. In addition to those residual oils commercially employed as asphalt base materials, lubricating oil distillates and sol-

vent extracts resulting from the treatment of various petroleum fractions with such selected solvents as phenol, nitrobenzene, B,B'dichloroethylether (Chlorex), SO_2, etc., either alone or in combination with other high molecular weight petroleum fractions such as the residual oils or lubricating distillates, may be oxidized in accordance herewith to produce asphaltic products suitable for a wide range of uses. And whereas the present invention is particularly adapted to the production of waterproofing asphalts and the like, it should be apparent that a wide range of stocks may be handled to produce a variety of asphalt products.

For purposes of illustrating the oxidation of a typical Wyoming sour crude residual oil to produce an excellent canal lining asphalt, the following example is set forth.

EXAMPLE

120 tons of a Wyoming crude residual oil resulting from the atmospheric and vacuum reduction of a sour Wyoming crude mixture was charged to a horizontal steel tank 14 feet in diameter by 14 feet long and heated to a temperature between 440° and 460° F. About four tons of the same stock was charged to a steam jacketed slurry tank equipped with a mixing impeller, gear pump, and circulating lines, and heated therein to a temperature of about 325° F. After such temperature was attained, powdered P_2O_5, in an amount sufficient to give an ultimate catalyst concentration when the catalyst slurry was admixed with the main charge of about 1.1%, was then vigorously admixed with the oil. The concentration of catalyst in the slurry was about 17.5% by weight. The mixture of oil and catalyst was stirred vigorously for about one hour. At the conclusion of this period, the slurry was smooth and homogeneous. Air introduction to the 120 tons of oil was begun and continued for a period of about 15 minutes. At the conclusion of this 15 minute period, the introduction of the catalyst slurry was begun while continuing the air introduction. Mechanical agitation of the slurry was continued throughout the slurry addition period. The air was introduced to the main charge at the rate of about 6 cubic feet per minute per ton of oil and vigorous agitation was maintained throughout the body of the oil at all times. The catalyst slurry was added slowly at a temperature of about 325° F. by means of a nozzle designed to spread as much of the slurry over the surface of the oil as is practicable. The introduction of the slurry was regulated so as to take place over a period of about four to five hours. Rapid introduction of the slurry rather than slow addition, preferably by a nozzle as described, has inevitably resulted in a carbon tetrachloride solubility below 97% and in some instances the product has been unfilterable after dispersion in the solvent.

In Table I are set forth data demonstrating the effect of varying the critical features of the present process. Thus, is shown the effect of failing to have the main body of the oil heated to oxidation temperature prior to the introduction of the catalyst slurry. This is shown for both slow and rapid addition of the slurry. It will be noted that products having improved solubilities also exhibit greater modification in penetration for a given softening point. On the other hand, data are provided which demonstrate the disadvantage of introducing this catalyst slurry too rapidly even though the main body of the oil is maintained at oxidation temperature. While the interdependence of the requirements that a residual oil be brought to oxidation temperature before catalyst addition and slow addition of the catalyst slurry is not entirely understood, it is obvious from these data that they are dependent and that without observing both of these requirements, the consistent production of satisfactory blown asphalt from a crude such as is employed is impossible. And, whereas, the solubility in carbon tetrachloride is particularly susceptible to change when the present process is not employed, variation of one or more features of the process often results in failure to pass certain other important specifications. By observing the requirements of the present process, however, excellent products are readily obtainable. It should be noted in Table 1 (run No. 2) that a slurry addition time of one-half hour has been employed on a laboratory scale to produce an asphalt which, although failing slightly the penetration specification at 77° F., passed the CCl_4 solubility specification. This was found to be the case in several laboratory experiments but not so on a large plant scale. The problem appears to be one of mixing and excellence of contact, i.e. a beaker may be much more readily stirred than a large still containing many tons of oil. Accordingly, as indicated above, at least an hour is required in practical operation, and preferably from about one and one-half hour to two hours but in small volume oxidations, slurry additions of between one-half hour and an hour may sometimes be employed. Furthermore, with respect to the excellence of contact it has been found that the better the spray and the greater the area of contact of slurry with hot oil, the more consistent the production of products meeting specification. A typical specification, viz. that of the U.S. Bureau of Reclamation referred to above, is as follows:

Softening point, ° F	175–200
Penetration at 77° F	50–60
Penetration at 32° F	NLT 30
Penetration at 115° F	NMT 120
Ductility at 77° F	NLT 3.5
Solubility in CCl_4	NLT 97

Table I

Run Number	1 [1]	2 [1]	3 [1]	4 [1]	5 [2]	6 [2]	7 [2]
Viscosity at 180° F. of charge (SSF).	214	124	214	124	124	170	300.
Weight of Total Batch	1,200 gm	1,600 gm	1,600 gm	1,760 gm	75 tons	60 tons	60 tons.
Percent P_2O_5 in Total Batch	1.25	1.0	1.0	1.25	1.25	1.25	1.25.
Percent P_2O_5 in Slurry	18.5	20.0	10.0	19.6	21.0	20.0	20.0.
Slurry Temperature	200°	300–350°	300–350°	225–250°	310°	310°	320°.
Pre-Air Blow [3]	3 min	3 min	3 min	5 min	15 min	50 min	45 min.
Air Rate	3 l./min./gm.	3.5 l./min./gm.	3.5 l./min./gm.	3.5 l./min./gm.	6.7 c.f.m./ton	14.7 c.f.m./ton.	12.8 c.f.m./ton.
Duration of Slurry Addition	Rapid [4]	0.5 hr.	1 hr.	Rapid [4]	1 hr.	1.3 hrs.	2.25 hrs.
Still Temperature During Addition.	460° F.	440° F.	440° F.	225–250° F.	305–325° F.	438–450° F.	450–460° F.
Oxidation Temperature	460° F.	440° F.	440° F.	460° F.	460° F.	440° F.	460° F.
Length of Air Blow	7 hrs.	7.5 hrs.	7.6 hrs.	7 hrs.	37 hrs.	21.5 hrs.	26 hrs.
Inspections of Final Product:							
Softening Point, ° F.	184	194	188	178	182	197	181.
Penetration at 77° F.	64	61	57	62	43	59	54.
Penetration at 32° F.		34	30		30	36	31.
Penetration at 115° F.		117	109		78	112	108.
Ductility at 77° F.		3.25	3.75	3.85	3.75	3.9	4.85.
Solubility in CCl_4, Percent	89.1	99.2	99.4	92.1	95.9	99.0	99.3.

[1] Laboratory runs.
[2] Plant runs.
[3] Before slurry addition begins.
[4] Introduced as rapidly as possible, e.g. no longer than 5 minutes.

The amount of catalyst employed in the oxidation of heavy oils to blown asphalts in accordance herewith should generally fall within the range of from about 0.1 to about 5.0 and preferably from about .75 to about 1.5% by weight of the total hydrocarbon charge. The slurry which is preferably formed from a portion of the main body of the residuum oxidized generally should comprise about 10 to about 25% catalyst and preferably from about 15 to about 20%. In any event, the slurry should have sufficient oil to permit adequate dispersion of the catalyst therein and yet not have too great an amount so as to dilute the catalyst to less than about a 10% concentration.

Air is introduced rapidly and in large quantities to the main body of the charge to both oxidize and agitate the same. Rates of air introduction of from about 6 to about 70 cubic feet of air per minute per ton and higher may be employed but it is generally found that an amount of air from about 6 to 15 cubic feet of air per minute per ton of charge gives excellent results in plant practice.

The product may, if desired, be blown with steam toward the end of the catalyst slurry addition to remove any objectionable odors from the oil. Since steaming has a slight adverse effect on the penetration-softening point relationship, it should be started before the product of desired softening point is obtained.

Percentages given herein and in the appended claims are by weight based upon the total hydrocarbon oil charge, unless otherwise specified.

In the appended claims, the phrase "high molecular weight petroleum hydrocarbons" is employed to designate the residual oils or base stocks which may be oxidized to a blown asphalt in accordance herewith. In connection with the use of such term, it will, of course, be understood that the heaviest of petroleum hydrocarbons are not high molecular weight in the sense that many polymers are high molecular weight, but with the possible exception of a paraffin wax, essentially any heavy petroleum oil or residuum of the type defined hereinabove may be employed. The phrase "heavy petroleum oil" is employed to designate the oil used in the catalyst slurry and may, as indicated above in accordance with the preferred embodiment of the present invention, comprise the same oil as that being oxidized. Likewise, it may comprise a different heavy petroleum oil. It should be understood, however, that although the terminology employed might indicate that the oil employed in the catalyst slurry and that being oxidized are different oils, such is not necessarily the case.

Having thus described our invention, what we claim as novel and desire to protect by Letters Patent is as follows:

1. The method of preparing an asphalt by catalytically oxidizing suitable high molecular weight petroleum hydrocarbons in the presence of a stable phosphorus-containing catalyst selected from the group consisting of phosphorus pentoxide, stable sulfides of phosphorus, and red phosphorus to produce a blown asphalt having good softening point, penetration, and ductility characteristics and high carbon tetrachloride solubility, which method comprises heating, prior to the addition of said catalyst, said high molecular weight petroleum hydrocarbons to oxidation temperature of from about 440° F. to about 500° F., contacting said high molecular weight hydrocarbons with air while at such oxidizing temperature, continuing introduction of air while admixing a fluid homogeneous slurry of said catalyst in a heavy petroleum oil, with said high molecular weight petroleum hydrocarbons over a period of at least about one hour, the amount of said stable phosphorus containing catalyst admixed being from about 0.1% to about 5.0% based upon the total weight of said high molecular weight petroleum hydrocarbons and said heavy petroleum oil, and continuing the introduction of air to the mixture until the desired softening point is attained.

2. The method of claim 1 wherein the stable phosphorus-containing catalyst is phosphorus pentoxide and the heavy petroleum oil employed to slurry said catalyst is a portion of said high molecular weight hydrocarbons.

3. The method of preparing an asphalt by oxidizing suitable high molecular weight petroleum hydrocarbons in the presence of phosphorus pentoxide to produce a blown asphalt having good softening point, penetration, and ductility characteristics and high carbon tetrachloride solubility, which method comprises heating, prior to the addition of said phosphorus pentoxide, said high molecular weight petroleum hydrocarbons to an oxidizing temperature of about 460° F., contacting said high molecular weight hydrocarbons with air while at such oxidizing temperature, continuing introduction of air while admixing a fluid homogeneous slurry of said phosphorus pentoxide in a heavy petroleum oil with said high molecular weight petroleum hydrocarbons over a period of time of about at least one hour, the amount of said phosphorus pentoxide admixed being from about 0.1% to about 5.0% based upon the total weight of said high molecular weight petroleum hydrocarbons and said heavy petroleum oil, and continuing the introduction of air to the mixture until the desired softening point is attained.

4. The mehod of claim 3 wherein the fluid homogeneous slurry of phosphorus pentoxide in a heavy petroleum oil is spread over a substantial area of the heated high molecular weight petroleum hydrocarbons during the introduction of air.

5. The method of claim 3 wherein the heavy petroleum oil employed to slurry the phosphorus pentoxide is a portion of said high molecular weight petroleum hydrocarbons.

6. The method of claim 3 wherein said high molecular weight petroleum hydrocarbons consist essentially of a sour Wyoming residual oil.

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