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PROCESS FOR OXIDIZING ASPHALT

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This invention relates to the manufacture of oxidized or air-blown asphalt from petroleum, petroleum residuum and the like.

It is well known to produce oxidized asphalt by blowing petroleum oils, such as petroleum residua, with air or other oxygen-containing gases at elevated temperatures for a sufficient period of time until the desired change in melting point is obtained. Air-blowing the petroleum oil has the effect of raising the melting point, lowering the penetration and ductility and also lowering the susceptibility of the asphalt to temperature changes, thus rendering the asphalt particularly suitable for roof coating, waterproofing and similar purposes requiring a bituminous material of high melting point and low temperature susceptibility. However, this older method of producing oxidized asphalt is very tedious and requires considerable time, often taking as much as 20 to 40 hours of blowing time in order to produce the asphalt of desired melting point-penetration characteristics.

It is among the objects of my invention to provide a process for producing oxidized asphalt wherein it is possible to accelerate the oxidation reaction time over that customary in asphalt production and at the same time producing asphalts of superior characteristics.

I have found that air-blowing petroleum oil in the presence of a relatively small amount of certain types of compounds catalyzes the oxidation reaction to such extent that the air-blowing time is considerably shortened. In accordance with my invention, a relatively small amount, i. e. 0.1 to 2% by weight of an organic complex of a metallic salt is added to the petroleum stock to be subjected to air-blowing and the mixture is subjected to air-blowing in the usual manner, preferably at elevated temperatures of approximately 350–550° F., until an asphalt is produced having the desired melting point and penetration. Air-blowing the petroleum stock in the presence of a small amount of the organic complex of a metallic salt will not only shorten the time required to produce an asphalt of high melting point but will also produce an asphalt of a higher penetration and ductility for a given melting point than can be obtained by air blowing, under similar conditions, the same petroleum stock without the addition of the organic complex of a metallic salt.

Organic complexes of metallic salts which may be employed in accordance with my invention include the sludges obtained in treating petroleum fractions with metallic salts, such as metallic halides, carbonates and sulfates. I have found the sludges obtained by treating petroleum fractions with metallic halides to be particularly desirable for this purpose. The sludge obtained in treating a cracked gasoline with aluminum chloride has been found to be particularly suitable in accelerating the oxidation reaction and in producing an asphalt of superior characteristics. Hydrocarbon stocks from which the organic complexes of metallic salts may be produced include the various hydrocarbon fractions containing hydrocarbons which are reactive with the metallic salts and particularly containing olefinic hydrocarbons. These include cracked gasoline, kerosene, gas oil, etc., polymer gasoline, kerosene and the like and also olefins produced from high molecular weight hydrocarbons such as wax, foots oil and the like. The latter are generally produced by halogenating a petroleum wax such as with chlorine at an elevated temperature and then dechlorinating the chlorinated hydrocarbons by heating to a higher temperature to produce the olefins. The sludges obtained by treating these olefins with aluminum chlorine are useful for the purpose of my invention.

The treatment of the hydrocarbons with the metallic salts to produce the sludge is well known in the art. In general, this includes adding a relatively small amount, i. e. 2%-10% by weight of the metallic salt to the stock to be treated and heating the mixture to a temperature generally around 100–600° F. Also, useful in my process are sludges obtained by cracking petroleum hydrocarbons, preferably in the liquid phase, in the presence of metallic salts, such as aluminum chloride, sludges obtained in the isomerization of hydrocarbons such as butane, pentane and naphtha in the presence of aluminum chloride, sludges obtained in the alkylation of isoparaffins with olefins in the presence of such alkylating catalyst as boron trifluoride, etc.

I have found the metallic halides to be particularly suitable to treat hydrocarbons to produce the organic complexes of the metal salts. These include the aluminum, zinc, iron, boron, tin, copper, antimony and boron chloride, fluoride, bromide, etc. Of these, the metallic chlorides are preferable, particularly aluminum chloride.

The invention may perhaps be better understood from the following example:

A petroleum residuum obtained from a San Joaquin Valley asphaltic crude oil and having a viscosity of 101 seconds Saybolt furol at 210° F. and a flash point of 430° F., Cleveland open cup, was placed in a vertical still provided with a

spider at its lower extremity for the introduction of air or other oxygen-containing gas. The residuum was heated to a temperature of about 280° F. and then about 1.5% by weight, based on the residuum, of an organic complex of aluminum chloride was mixed with the heated residuum. The blend was subjected to air-blowing at a temperature of about 480–490° F. for about 14.5 hours employing air at a rate of 2 cubic feet per minute per barrel of charge of residuum.

The organic complex of aluminum chloride was produced by mixing about 20% by weight of anhydrous aluminum chloride and 80% by weight of a polymer gasoline having a boiling range of about 150–250° F. and produced by polymerizing low boiling olefins such as butylene in the presence of phosphoric acid. The mixture was then heated for about 36 hours at a temperature of about 150° F. and the resulting sludge was separated from the treated gasoline by decantation.

The oxidized asphalt produced at the end of about 14.5 hours of air-blowing had a melting point of 208° F., penetrations of 9, 17 and 32 at 32, 77 and 115° F., respectively, a flash point of 440° F. (Cleveland open cup), a ductility of about 3.2 cm. at 77° F. and solubilities of 99.89, 99.11 and 66.6 in carbon bisulfide, carbon tetrachloride and 82° naphtha, respectively.

For comparison, another charge of the above San Joaquin Valley residuum was air-blown under similar conditions in the absence of the organic complex of aluminum chloride to approximately the same melting point of about 208° F. This required about 23 hours and produced an asphalt having penetrations of 5, 10 and 15 at 32, 77 and 115° F., respectively, a flash point of 445° F. (Cleveland open cup), a ductility of about 1.1 cm. at 77° F. and solubilities of 99.93, 99.92 and 63.9 in carbon bisulfide, carbon tetrachloride and 82° naphtha, respectively.

The comparative run indicates that a superior melting point-penetration-ductility relationship characteristic is obtained by air-blowing the charge in the presence of the organic complex of aluminum chloride.

The foregoing description of my invention is not to be taken as limiting but merely as illustrative thereof since many variations may be made by those skilled in the art without departing from the scope of the following claims.

I claim:

1. A process for producing asphalt which comprises incorporating a relatively small amount of a hydrocarbon complex of a metal halide in a petroleum oil fraction and commingling said oil fraction with oxygen-containing gas at an elevated oxidizing temperature.

2. A process for producing asphalt which comprises incorporating a relatively small amount of a hydrocarbon complex of a metal halide in a petroleum oil fraction and commingling said oil fraction with oxygen-containing gas at an elevated oxidizing temperature, a hydrocarbon complex of a metal halide being produced by treating a hydrocarbon oil with a metal halide.

3. A process for producing asphalt which comprises incorporating 0.1 to 2% by weight of a hydrocarbon complex of a metal halide in a petroleum oil fraction and commingling said oil fraction with oxygen-containing gas at an elevated oxidizing temperature.

4. A process for producing asphalt which comprises incorporating a relatively small amount of a hydrocarbon complex of a metal halide in a petroleum oil fraction and commingling said oil fraction with oxygen-containing gas at a temperature of approximately 350–550° F.

5. A process for producing asphalt which comprises incorporating in a petroleum oil fraction a relatively small amount of a sludge obtained by the treatment of a hydrocarbon oil with a metal halide and commingling said oil fraction with oxygen-containing gas at an elevated oxidizing temperature.

6. A process for producing asphalt which comprises incorporating a relatively small amount of a hydrocarbon complex of an aluminum halide in a petroleum oil fraction and commingling said oil fraction with oxygen-containing gas at an elevated oxidizing temperature.

7. A process for producing asphalt which comprises incorporating a relatively small amount of a hydrocarbon complex of an aluminum halide in a petroleum oil fraction and commingling said oil fraction with oxygen-containing gas at an elevated oxidizing temperature.

8. A process for producing asphalt which comprises incorporating a relatively small amount of a hyrocarbon complex of aluminum chloride in a petroleum oil fraction and commingling said oil fraction with oxygen-containing gas at an elevated oxidizing temperature.

9. A process for producing asphalt which comprises incorporating in a petroleum oil fraction a relatively small amount of a sludge obtained by the treatment of a hydrocarbon oil with an aluminum halide and commingling said oil fraction with oxygen-containing gas at an elevated oxidizing temperature.

10. A process for producing asphalt which comprises incorporating in a petroleum oil fraction a relatively small amount of a sludge obtained by the treatment of a hydrocarbon oil with an aluminum halide and commingling said oil fraction with oxygen-containing gas at an elevated oxidizing temperature.

11. A process for producing asphalt which comprises incorporating in a petroleum oil fraction a relatively small amount of a sludge obtained by the treatment of a hydrocarbon oil with aluminum chloride and commingling said oil fraction with oxygen-containing gas at an elevated oxidizing temperature.

12. A process for producing asphalt which comprises incorporating in a petroleum oil fraction a relatively small amount of a sludge obtained by the treatment of cracked gasoline with a metal halide and commingling said oil fraction with oxygen-containing gas at an elevated oxidizing temperature.

13. A process for producing asphalt which comprises incorporating in a petroleum oil fraction a relatively small amount of a sludge obtained by the treatment of a hydrocarbon oil with an aluminum halide and commingling said oil fraction with oxygen-containing gas at an elevated oxidizing temperature.

14. A process for producing asphalt which comprises incorporating in a petroleum oil fraction a relatively small amount of a sludge obtained by the treatment of a hydrocarbon oil with aluminum chloride and commingling said oil fraction with oxygen-containing gas at an elevated oxidizing temperature.

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