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(54) Process for preparing modified asphalts.

(57) An asphalt is modified by mild oxidation, with for example, air, oxygen or hydrogen peroxide, at a temperatur of 140°C to 170°C for up to one hour such that the softening point of the asphalt is not materially altered. Substantially reduced reactivity toward sulfur is imparted. Such a mildly oxidised asphalt can be treated immediately with sulfur at a temperature of 120°C to 170°C form a sulfur modifier product. Alternatively, the mildly oxidised product can be stored hot and subsequently treated with sulfur, for example, at a road-making site, without the high hydrogen sulfide evolution often encountered with known products.

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This invention relates to a process for preparing modified asphalts. The term asphalt is employed herein synonymously with the term bitumen.

It is known that the addition of sulfur to asphalt leads to modified binders having improved workability and mechanical characteristics. However, the blending operation, which must take place above 120°C(melting point of sulfur), is generally accompanied by the evolution of significant amounts of H_2S. This is due to the reaction of sulfur with some molecules of the asphalt blend which are especially prone to it.

It is an object of the present invention to provide an improved asphalt, which when treated with sulfur gives rise to decreased, or no, H_2S evolution.

According to one aspect of the present invention there is provided a process for modifying asphalt by contacting the asphalt with an oxidant, optionally in the presence of a catalyst, wherein the asphalt is contacted with a liquid or gaseous oxidant at a temperature of 140°C to 170°C for a period up to one hour, such that the softening point of the asphalt is not materially altered and the reactivity of the asphalt toward sulfur is decreased.

It has been found that solid oxidants, for example, chromium trioxide and phosphorus pentasulfide are not suitable for use in invention. A suitable liquid oxidant is hydrogen peroxide. Preferably, however, the oxidant is air or oxygen.

The temperature of contact is in the range 140°C to 170°C, more especially 145°C to 155°C. It is preferred that the duration of the contact is not more than one hour, typically 10 to 20 minutes depending on the feedstock being processed. In accordance with the invention the product is one in which the softening point of the starting material is not significantly altered.

Thus, the product of such a process is a deliberately mildly oxidized asphalt and hence is very different from the well-known oxidized or "blown" asphalt products which are normally prepared by oxidation for from 4 to 8 hours at 240°C to 290°C. The product is also very different from that disclosed in United Kingdom Patent 278,679 published in 1928. The disclosure there is of a tar, tar oil or anthracene oil oxidised with air, or a liquid oxidant such nitric acid, to an extent that the product (i) retains a sufficient degree of fluidity (ii) is insensitive to water, so that it can be directly used in road construction.

Whilst it can have other uses, the mildly oxidised product of the present invention is especially suitable for the preparation of asphalt/sulfur/ materials, preferably with sulfur which is not chemically bound or combined.

According to another aspect of the invention, a sulfur-modified asphalt is obtained by blending the mildly oxidised product with sulfur at a temperature in the range 120°C to 170°C. The steps of contacting with the oxidant and with the sulfur are preferably conducted at substantially the same temperature in the range 140°C to 170°C, more especially 145°C to 155°C. The step of contacting with sulfur need not necessarily immediately follow the mild oxidant but can, if desired, follow later, for example, at a road-making site.

The sulfur may be employed in amount from up to 45 wt%, more especially 30 wt %.

The asphalt feedstock employed in processes of the invention may be any one of the known non-oxidized materials, for example, the penetration grade asphalts such as 40/60 to 180/220, preferably 80/100. However, such softer petroleum residua can be employed, for example, those with penetrations of about 600, or higher, including the light 600-800 grade (ASTM D 5).

The invention will now be illustrated by reference to the following Examples:-

Example 1 In this example ten different asphalt types were tested with respect to their reactivity with sulfur. The reactivity was quantified by the cumulative quantity of H_2S evolved during the first ten minutes of treatment of the asphalt with elemental sulfur at 150°C.

Table 1 shows for each material its crude oil origin, its penetration and the said H_2S quantity evolved.

The first six materials show essentially the same reactivity to sulfur, independent of the crude oil origin. Moreover, as indicated by Tests 2 and 3, the reactivity is substantially independent of the penetration, so that short and long run vacuum residua produced from the same crude oil behave substantially similarly when treated with the sulfur.

Tests Nos 7 and 8 were conducted with two different blends of straight run vacuum residua and oxidized vacuum residua, that is to say the normal fully oxidized material. The blends show less reactivity with sulfur under the stated conditions.

Finally, Tests 9 and 10 were conducted with two mildly blown materials made in accordance with the invention. Both materials show a considerably reduced reactivity with sulfur under the stated conditions, the origin of crude oil being unimportant. It will be seen that the reactivity is appreciably less than even the blends 7 and 8; indicating that the results obtainable by means of the invention cannot be achieved by mere blending of known blown and un-blown materials.

Example 2 In order to illustrate suitable conditions for conducting the mild oxidation, a series of air blowing experiments was conducted on some asphalt materials at 150°C or 165°C and for oxidation times in the range 5 to 60 minutes. The asphalts employed were (1) a straight run vacuum residuum from an Arabian Light crude (2) a blend of straight run vacuum residuum having a penetration 80 to 100 and (3) a straight run vacuum residuum of penetration 80 to 100 from an Arabian Heavy crude oil.

Fig 1 is a plot of relative reactivity of the various oxidized materials thus produced with sulfur, against oxidation time. With all materials H_2S is reduced by 50% after only 15 mins air blowing, and by 75% after 1 hour.

Similar results were obtained employing hydrogen peroxide as the oxidant. By contrast NH_4NO_3, CrO_3 and P_2O_5 do not produce similar results.

Example 3 This example illustrates that the mildly oxidized product of the invention retains its low reactivity to sulfur over a storage period at 150°C of ten or more days. This is very important in practice in that the oxidized product can be made and hot-stored in one location and thereafter blended with sulfur at another location days later.

Fig 2 shows the results obtained with an asphalt of penetration 80 to 100 from an Arabian Heavy crude and a residue from the vacuum distillation of an Arabian Light crude. The figure clearly shows that even after 10 days storage, both products are still considerably less reactive with sulfur then the corresponding unblown materials.

The sulfur-modified, mildly oxidized asphalts of the invention have considerable importance as binding agents in road-making and road-surfacing operations, among other uses. H_2S evolution has hitherto presented problems which sometimes rule out the possibility of using sulfur-modified asphalts even though they have desirable properties. By means of the invention H_2S evolution can be reduced, thereby widening the practical scope of use of sulfur-modified asphalts, since the important properties of those are not significantly affected in the products according to the present invention.

TABLE 1

TEST No.	CRUDE OIL ORIGIN	ASPHALT TYPE	PENETRATION (ASTM D5)	H_2S EVOLVED IN FIRST 10 MINS (ml/kg)*
1	ARAB LIGHT	ALL ARE	600	255
2	ARAB HEAVY	STRAIGHT	90	295
3	ARAB HEAVY	RUN VACUUM	45	305
4	TIA JUANA	RESIDUA	90	255
5	CRUDE OIL BLEND		90	340
6	CRUDE OIL BLEND		45	303
7	ARAB HEAVY	BOTH ARE BLENDS OF STRAIGHT RUN AND OXIDIZED VACUUM RESIDUA	70	207
8	ARAB HEAVY		50	225
9	ARAB LIGHT	VACUUM RESIDUA MILDLY BLOWN PER INVENTION	90	185
10	ARAB LIGHT		45	165

* AFTER TREATMENT WITH 20 wt% S at 150°C.

CLAIMS:

1. A process for modifying asphalt by contacting the asphalt with an oxidant, optionally in the presence of a catalyst, characterised in that the asphalt is contacted with a liquid or gaseous oxidant at a temperature of 140°C to 170°C for a period up to one hour, such that the softening point of the asphalt is not materially altered and the reactivity of the asphalt toward sulfur is decreased.

2. A process as claimed in claim 1, wherein the oxidant is oxygen or air.

3. A modified asphalt whenever prepared by either of the preceding claims.

4. A process for preparing a sulfur-modified asphalt, characterised by contacting the modified asphalt claimed in claim 3 with non-chemically-combined or bound sulfur, in the temperature range 120°C to 170°C.

5. A process as claimed in claim 4, wherein the contacting with the sulfur follows substantially immediately after the contacting with the oxidant.

6. A process as claimed in claim 5, wherein the steps of contacting with the oxidant and with the sulfur are both conducted at substantially the same temperature, which temperature is in the range 140°C to 170°C, preferably 145°C to 155°C.

7. A sulfur-modified asphalt whenever produced by the process claimed in any one of claims 4 to 6.

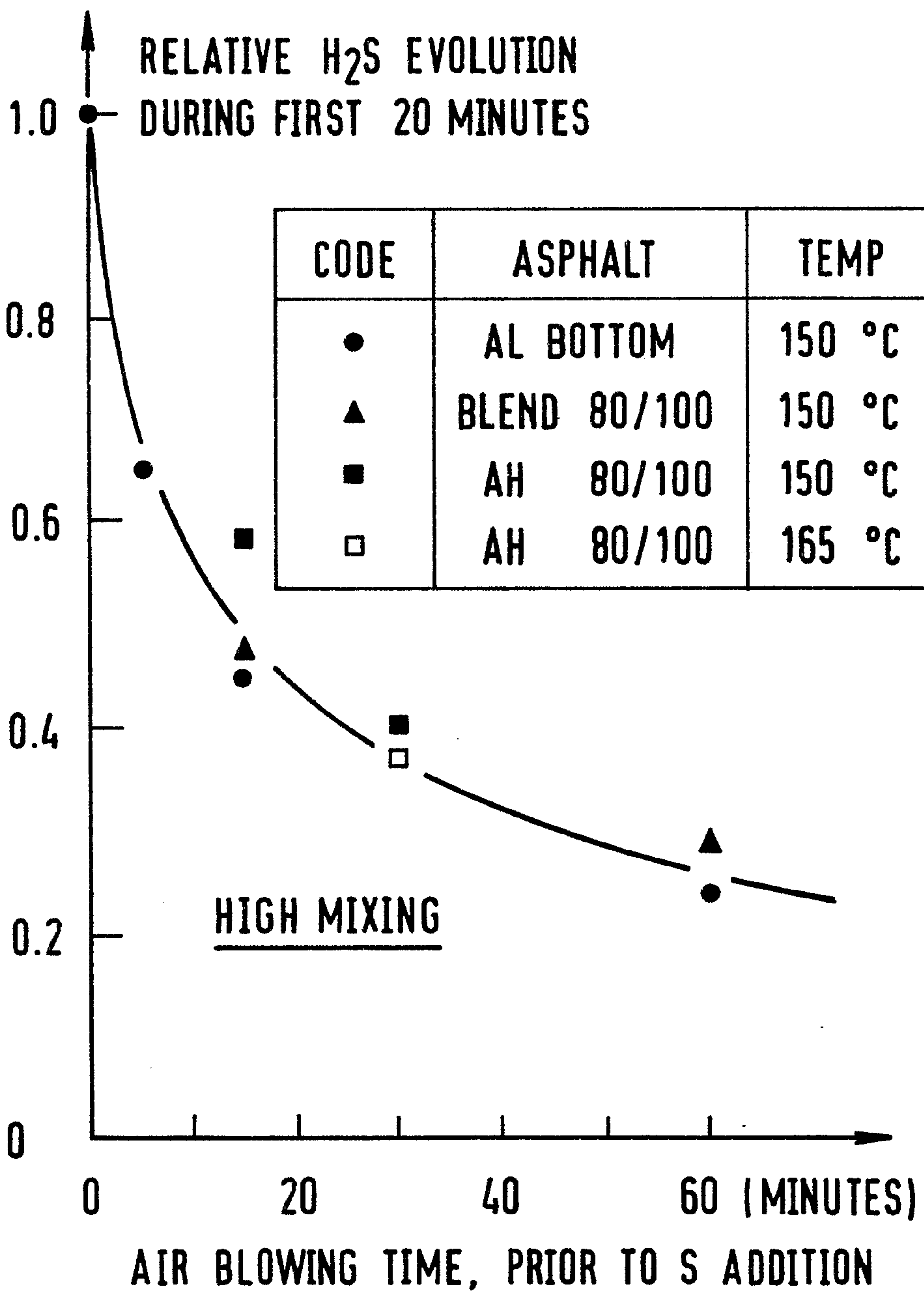
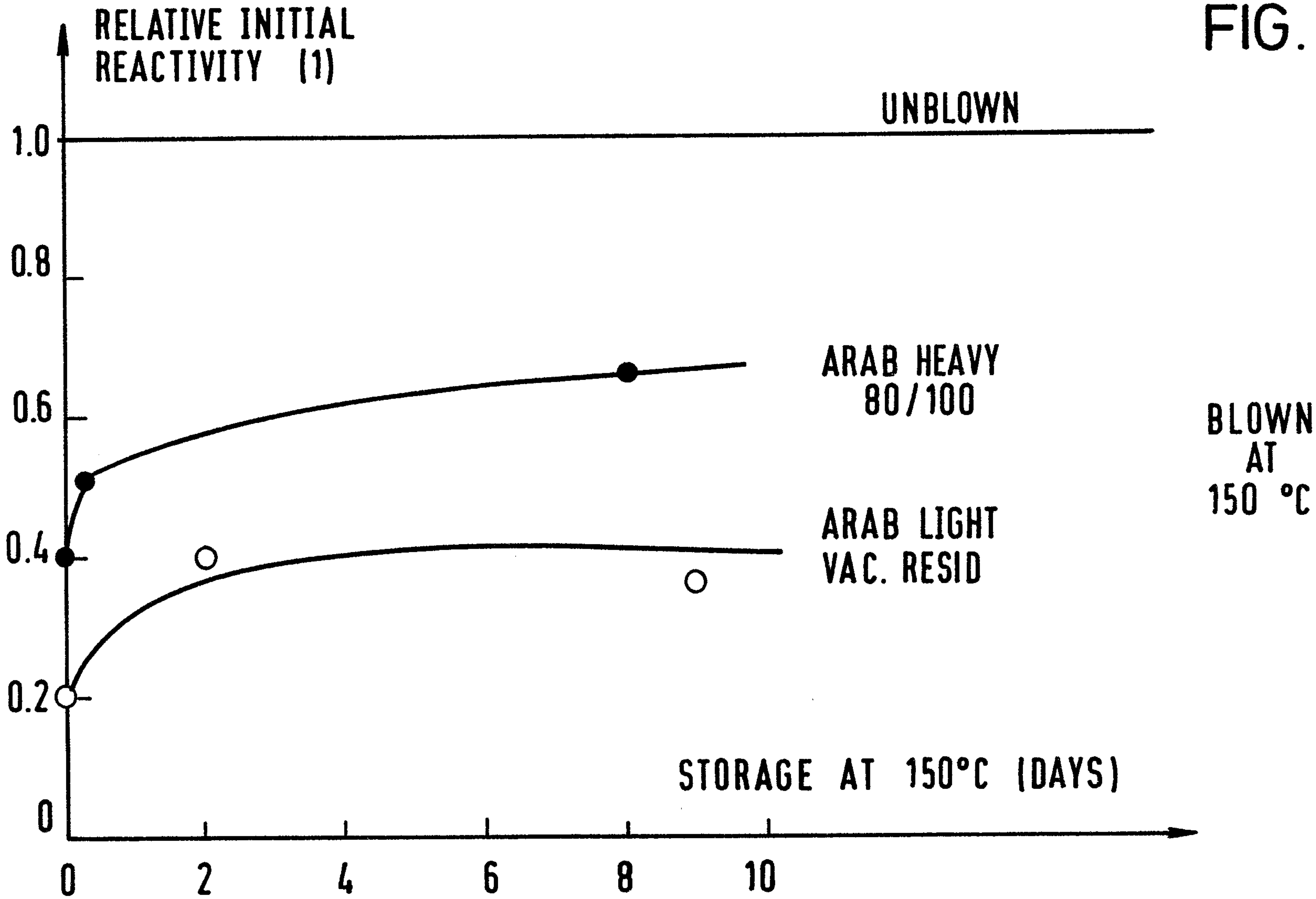

RELATIVE H_2S EVOLUTION
DURING FIRST 20 MINUTES
1.0
0.8
0.6
0.4
0.2
0
CODE
ASPHALT
TEMP
AL BOTTOM
150 °C
BLEND 80/100
150 °C
AH 80/100
150 °C
AH 80/100
165 °C
HIGH MIXING
0
20
40
60 (MINUTES)
AIR BLOWING TIME, PRIOR TO S ADDITION

FIG. 1

FIG. 2



(1) RATIO OF H_2S EVOLVED IN 20 MINUTES AT 150°C FROM 20/80 SULPHUR/ASPHALT BLENDS (WITH AND WITHOUT MILD BLOWING)