3,418,402
Patented Dec. 24, 1968

3,418,402

PROCESS OF MAKING A COMPACTED STRUCTURAL ELEMENT IN A MOIST ATMOSPHERE

Robert R. Grissom, Colonia, Edward K. Matthews, Westfield, and Werner Kurzbuch, Elizabeth, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Filed Feb. 26, 1965, Ser. No. 435,682
4 Claims. (Cl. 264—65)

ABSTRACT OF THE DISCLOSURE

Process for producing a strong structural element comprising a bituminous binder and an aggregate by heat curing the same in an initial stage and thereafter contacting the cured product with moist air such as steam.

This invention is directed to a solid bituminous-aggregate composition of enhanced structural strength. In particular, this invention is directed to a process of producing a solid, compressed bituminous-aggregate structural element which has superior structural performance characteristics and to the element produced by such process. More particularly, this invention is directed to a process of treating an aggregate-bituminous structural element at a high temperature in an atmosphere having water therein and to such structural element.

Structural elements made of a binder such as a bituminous material and an aggregate are well-known in the art. Various methods are known to the art for improving the structural characteristics of such elements. However, one problem has not been overcome, that is, the tendency of the element to change shape or to contract at some time remote to the time of manufacture. This problem is quite striking when the elements form an integral part of the structure at the time they change shape or shrink. In such a situation, it can readily be seen that the structure can literally tear itself apart. Such a dramatic effect may not take place but cracks and crevices will appear in the structure which will decrease the strength of the structure.

It has now been found that structural elements consisting essentially of a bituminous binder and an aggregate can be produced so that any change subsequent to the time of manufacture will be negligible. In accordance with the present invention, a binder material and an aggregate are mixed, pressed into shape, heat treated at a temperature of from 212° to 500° F. for from 4 to 32 hours, then treated in a moist atmosphere at a temperature of 225° to 500° F. for from 1 to 80 hours and then cooled to ambient temperature. Preferably, the pressed article is heated to 225° to 350° F. for from 4 to 20 hours.

In the practice of the present invention, any of the known binders may be used such as coal tar derivatives and petroleum base bituminous materials. The binder materials can also consist of mixtures of various bituminous materials and mixtures of bituminous materials with synthetic resins.

The binder can be any of the known binders such as that family of materials commonly referred to as asphalts, such as natural or petroleum residua of thermoplastic solid or semisolid consistency at ambient temperatures, normally of brown to black cementitious material in which the predominating constituents are bitumens. The bituminous material to be used may be selected from a wide variety of natural and industrial products. For instance, various natural asphalts may be used such as natural Trinidad, gilsonite, Grahamite and Cuban asphalts. Petroleum asphalts suitable for the purposes of this invention include those asphalts obtained from California crude, from tar sands, Venezuelan or Mexican petroleum asphalt or a Middle East or Mid-Continent airblown oil and the like, or combinations thereof. Petroleum asphalts also include those asphalts derived from hydrocarbon feed stocks such as bitumen, asphaltic residua obtained in a petroleum refining process such as those obtained by the vacuum distillation of petroleum hydrocarbon crude oils, the solvent deasphalting of crude residuum fractions, tarry products from the chemical refining such as oxidation of high molecular weight hydrocarbons, those asphalts obtained from hydrogenated coal products, the asphaltic material obtained in the thermal or catalytic cracking of petroleum to obtain gasoline or other light fractions or any combination of these materials.

Although the petroleum asphalts are preferred, other suitable bituminous material would include coal tar, wood tar and pitches from various industrial processes. The invention can also be successfully practiced with chemically modified asphalts such as halogenated, e.g., chlorinated or sulfurized or phosphosulfurized asphalts, as well as asphalts treated with epoxides or haloepoxides like ethylene oxide and epichlorohydrin, or with silane halides, nitrobenzene, chlorinated aliphatics such as carbon tetrachloride and halohydrocarbons such as methylene chloride and the like. Additionally, the asphalts can be mixed in major or minor amounts, e.g., 1 to 10 wt. percent with other natural and synthetic thermoplastics and thermosetting materials like rubbers, resins, polymers and elastomers of an oil, resinous or rubbery nature. Nonlimiting examples of suitable materials include polyolefins, polypropylene, polyethylene, polyisobutylene and the like; natural or synthetic rubber like butyl rubber, halogenated butyl rubber, polydienes like polybutadiene, elastomeric copolymers of styrene and butadiene, copolymers of ethylene and propylene, and the like; epoxy resins; polyalkylene oxides; natural and synthetic waxes; polyvinyl acetates; phenol aldehyde condensation products; and the like and combinations thereof.

Furthermore, in a modification wherein the asphalt is chemically modified by reaction with liquid reagents, for example, CCl_4, the reagent liquid can often be used as the asphalt solvent, whereupon the desired reaction occurs before, after or during the compaction of the soil-asphalt cutback mixture or after or during the curing step, or the reaction may occur continuously during both finishing process steps.

Bitumen subjected to any of the commonly used petroleum or refining and treating processes such as distillation, steam reduction, solvent separation or blending, and the like can be employed. The invention is of particular value with oxidized asphalts, for example, those asphalts prepared by air blowing or chemically oxidizing asphaltic residua at elevated temperatures (400° to 500° F.) with or without the presence of catalytic reagents such as compounds of phosphorus (like phosphorus pentoxide) or of the transition metals (like ferric chloride). These oxidized asphalts commonly have ASTM softening points of at least 100° F., e.g., 100° to 300° F. or higher. Those asphalts and especially those oxidized asphalts and straight reduced asphalts having an ASTM softening point of 100° F. and above and an ASTM D–5 penetration at 77° F. of 315 or below are the preferred asphalts of the invention.

The foregoing bituminous materials are preferably applied to the pretreated solid in the form of a solvent cutback. The cutback solvent should preferably be one that is sufficiently volatile to be substantially volatilized during the selected curing step, i.e., a solvent having a boiling point of less than 600° F. or advantageously less than 400° F., such as a petroleum naphtha or other hydrocarbon solvent boiling within the range of about 175° to 600° F., e.g., 200° to 400° F. Suitable asphalt concentrations in the cutback solution are from 30 to 90 wt. percent asphalt, for example, 50 to 75 wt. percent. Preferably, the Furol viscosity at the temperature at which the cutback is applied should be 100 or less, e.g., 20 to 100 Furol. Suitable cutback solvents would thus include, but are not limited to, hydrocarbons such as toluene, benzene, xylene, Varsol, VM&P naphtha, halohydrocarbons such as carbon tetrachloride and methylene dichloride, or any combinations thereof.

The cutback asphalt compositions may contain other additive agents such as wetting and emulsifying agents and antistripping agents. The asphalt cutback should be used in an amount sufficient to provide at least 5 to about 30 wt. percent asphalt or higher based on the soil, with maximum comperssive strengths usually attained at 8 to 20 e.g., 10 to 14 wt. percent asphalt. The amount and character of the cutback solvent should be such that the cutback composition will have the proper coating viscosity, since the failure to thinly and uniformly coat a considerable majority, e.g., over 95%, of the solid particles will greatly affect the dry, and especially the wet strength of the resulting compacted object. A thick coating occasioned by a viscous asphalt cutback will be wasteful of materials and also tends to create low strength structures.

The solid aggregate of this invention can be any of the known prior art materials such as any dry inorganic or organic solid material, with earth and soil the economically preferred solid materials for the production of hard, dense structures useful in building construction. The solid aggregate material may comprise combinations of materails of natural or synthetic origin with or without the presence of clay-type soils. For example, combinations include 10 to 60% clay with iron ore fines, coke, graphite, or other material. Suitable nonlimiting examples of other aggregate materials include finely subdivided cinder, expanded slag or clay, rock wool, steel wool, abrasives, expanded clays, cellulose fibers, sawdust, can fibers, bagasse, hemp, jute, coke, iron ore, diatomaceous earths, clays, soil, slit, coal, asbestos, glass fibers, wood chips, quartz, carbonate rocks, volcanic ash, bamboo, and the like and combinations thereof.

In the practice of the instant invention, the binder material and the aggregate can be mixed either by mastication such as in a pug mill or by impact mixing both of which are well-known to the prior art. The mixing step can be conducted at ambient temperatures if a cutback asphalt is used or heated in order to melt the binder if such is in a solid state or the mixing can be conducted at an elevated temperature. After mixing, the materials are compressed into shape at ambient or elevated temperatures. Preferably, the compression is sufficient to produce an element which is between about 80 and 98% of its theoretical density. The compressed shaped element is then heat treated at a temperature of between about 350° and 500° F. for from 4 to 32 hours. The heat treated element is then placed in a moist atmosphere at an elevated temperature of from 225° to 350° F. for a time from about 4 to 20 hours. The treatment in a moist atmosphere can take place during the latter part of the heat treating step. For example, if the compressed element is to be heat treated for 16 hours at 400° F., a moist atmosphere is introduced during the last half, that is, during the last 8 hours of the treatment.

The moist atmosphere can either be steam introduced into the heat treating oven or can be water which is introduced into the oven which vaporizes due to the heat of the oven. The structural element must be kept in contact with the moist atmosphere for a minimum of one hour before cooling to ambient temperature. The total pressure during the moisture treating step can be any convenient pressure. However, an absolute pressure of 1 to 30 atmospheres is preferred. The moist atmosphere will comprise an atmosphere being from 25 to 100% saturated with water, preferably, 75 to 100% saturated with water.

In order to designate a suitable range of density (degree of compaction) for the development of high strength, an expression "Percent of Theoretical Density" has been formulated which is defined as follows:

Percent of Theoretical Density=percent of the density the solid+binder would have if there were no voids in the compacted structure.

A sample calculation would be: A compacted mixture of clay soil (d=2.61 g./cc.) with 10 wt. percent asphalt based on the soil (d=1.04 g./cc.) is found to have a density of 2.08 g./cc.

The theoretical density (no voids) of this mixture would be

$$\frac{100}{2.61}+\frac{10}{1.04}=\frac{110}{x}$$

$$x=2.29$$

$$\text{Percent of Theor. Den.}=\frac{2.08}{2.29}\times 100=90.8\%$$

With sandy clay soils containing about 20 to 25% clay (less than 0.005 mm. particle size) and 9 to 12% by weight asphalt, the desired percentage of theoretical density is usually within the range of 80 to 94%.

The following examples are submitted for illustration purposes only and are not to be construed as limitations upon the scope of the invention as set forth in the appended claims.

EXAMPLE 1

In order to demonstrate the effectiveness of the instant process, the following tests were made. The test elements were made by mixing 6 wt. percent asphalt with 94 wt. percent aggregate which was composed of a mixture of sand and limestone. The mixture was then pressed into brick shapes and cured at 400° F. for 16 hours. The cured bricks were then cooled to room temperature. After cooling, the bricks were exposed to cyclical moisture contact conditions during which they were placed in saturated steam at 15 p.s.i.g. and 250° F. for 5 hours; cooled to 75° F. in air at 100% relative humidity for 18 hours; measured; dried at 200° F. in air having a 5 to 10% relative humidity for 6 hours; again cooled in air at 75° F. at 30 to 50% relative humidity for 18 hours minimum and then remeasured. This cycle was repeated until there was no appreciable change in consecutive dry measurements (i.e., no further increase in permanent set). The results of this test are shown in Table I. As seen from Table I, the maximum elongation without vapor treating was 0.28%. The maximum elongation (moisture response) after vapor treating was 0.28%—0.19%=0.09%.

TABLE I.—RESULTS OF CYCLICAL STEAM SATURATION TEST

Cycle No.	Maximum elongation,[1] Percent	Permanent set,[2] percent	Reversible moisture response,[3] percent
1	0.13	0.09	0.04
2	0.19	0.12	0.07
3	0.21	0.14	0.07
4	0.21	0.15	0.06
5	0.24	0.17	0.07
6	0.25	0.18	0.07
7	0.25	0.18	0.07
8	0.27	0.18	0.09
9	0.27	0.18	0.09
10	0.28	0.19	0.09

[1] Maximum elongation, percent $=\frac{L_1-L_0}{L_0}\times 100.$

[2] Permanent set, percent $=\frac{L_2-L_0}{L_0}\times 100.$

[3] Reversible moisture response, percent $=\frac{L_1-L_2}{L_0}\times 100.$

L_0=initial length in inches (between measuring points) of specimen.
L_1=length in inches of specimen after exposure to 15 p.s.i.g. steam for 5 hours, and air at 75° F., 100% relative humidity for 18 hours.
L_2=length in inches of specimen after drying in air for 6 hours at 230° F., 5-10% relative humidity and cooling for 18 hours in air at 75° F., 30-50% relative humidity.

EXAMPLE 2

Various structural element compositions were tested in order to determine the effect of tempering thereon. These tests have shown that the amount of reduction of moisture response that can be effected by tempering and hence of "in use" stresses, is dependent upon the composition of the mix used to make the structural elements and specifically upon the types of soils and aggregates used. Data show that the moisture response of bituminous structural elements made of an aggregate in which the fines were composed of a minimum of clay and a maximum of crushed rock or other relatively inert materials can be reduced by a minimum of 50% by tempering the structural elements.

EXAMPLE 3

In order to demonstrate the large decrease in stress developed within structural elements during use which results from tempering heat cured asphalt-aggregate structural elements to structural elements consisting essentially of 8 wt. percent asphalt and 92 wt. percent aggregate, compositions such as set forth in Example 1 are pressed into shape and heat cured at 400° F. for 16 hours. One of the structural elements is then heat treated in a saturated atmosphere at 15 p.s.i.g. for 9 hours. The two structural elements are then cooled to room temperature and then tested in order to determine the internal stresses developed in each of the elements. The results of the tests are set forth in Table II.

Table II.—Water vapor treating reduces "in use" stresses

Case:	Stress developed, p.s.i.
(A) Without vapor treating	2240[1]
(B) With vapor treating[2]	720

[1] Stress calculated using Young's Modulus=8×10^5 p.s.i.
[2] Treating at 15 p.s.i.g. steam pressure.

Tests were also conducted in order to determine whether or not the heat curing step can be conducted in a moist atmosphere, that is, an atmosphere having more than 25% saturation with water. The results showed that the heat curing step could not be conducted in a moist atmosphere. Tests also showed that heat curing the elements, followed by a quick, cold-water quench did not increase the structural strength of the elements but did rather decrease the strength.

What is claimed is:

1. A process of making a highly compacted, strong structural element which comprises the steps of:
   (a) mixing a bituminous binder with an aggregate,
   (b) compacting the mixture to within 80 to 98% of its theoretical density,
   (c) heat curing the compacted mixture at a temperature of 350° to 500° F. for a time from 4 to 32 hours in the absence of moisture,
   (d) contacting the heat cured, compacted mixture with steam at 15 p.s.i.g. at a temperature of 225° F. for 8 to 20 hours, and
   (e) cooling the element to ambient temperature in the moist atmosphere.

2. A process of making a highly compacted, strong structural element which comprises the steps of:
   (a) mixing a bituminous binder with an aggregate,
   (b) compacting the mixture to within 80 to 98% of its theoretical density,
   (c) heat curing the compacted mixture at a temperature of 350° to 500° F. for a time from about 4 to 32 hours in the absence of moisture,
   (d) contacting the heat cured, compacted mixture with a moist atmosphere which is 75 to 100% saturated with water, at a temperature of from 212° to 500° F. for from 1 to 80 hours, and
   (e) cooling the element to ambient temperature in the moist atmosphere.
3. A process of making a highly compacted, strong structural element which comprises the steps of:
   (a) mixing 6 wt. percent Binder C asphalt with 94 wt. percent aggregate comprising a mixture of sand and limestone,
   (b) compacting the asphalt-aggregate mixture to about 90% of its theoretical density,
   (c) heat curing the compacted mixture at a temperature of about 400° F. for about 16 hours,
   (d) contacting the heat cured compacted mixture with a hot, moist atmosphere comprising steam at 15 p.s.i.g. at a temperature of 250° F. for 12 hours, and
   (e) cooling the heat cured, compacted mixture to ambient temperature.
4. Process as defined by claim 1 wherein said aggregate comprises a clay-type soil.

References Cited

UNITED STATES PATENTS

3,062,672	11/1962	Kerkhoven et al.	106—281
3,168,602	2/1965	Davies et al.	106—281 X
3,261,892	7/1966	Sommer et al.	106—281 X
3,281,256	10/1966	Rogers et al.	106—281
3,287,146	11/1966	Rogers et al.	106—281

JULIUS FROME, *Primary Examiner.*

J. B. EVANS, *Assistant Examiner.*

U.S. Cl. X.R.

106—38.8, 281, 282, 284; 260—38.5