Jan. 1, 1957 H. E. BOWERS 2,776,210

PROCESS FOR PRODUCING POROUS OIL SHALE PRODUCTS

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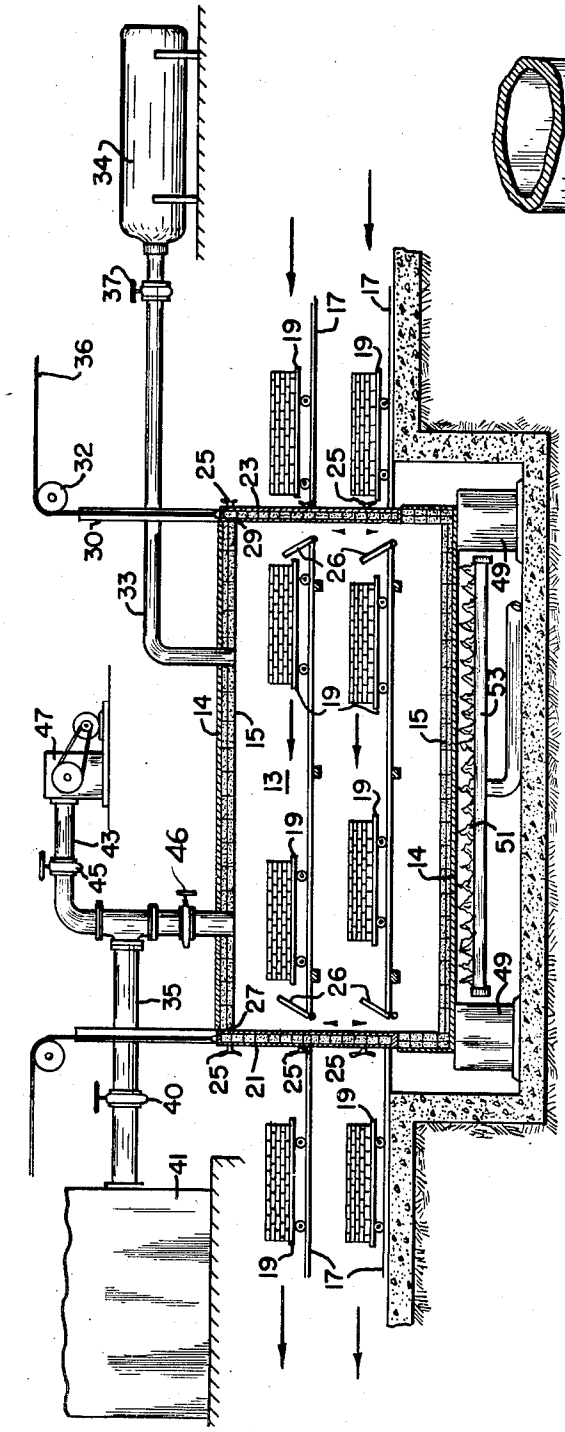


FIG.-1

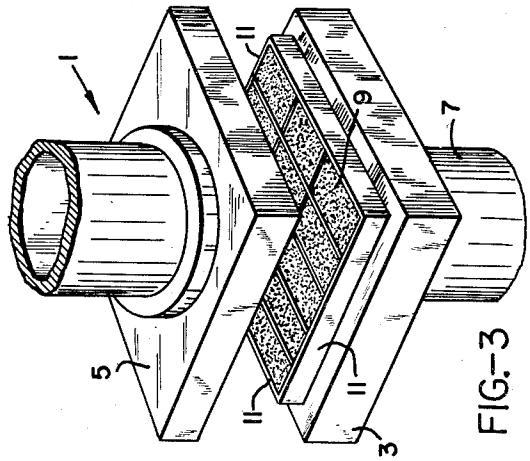


FIG.-3

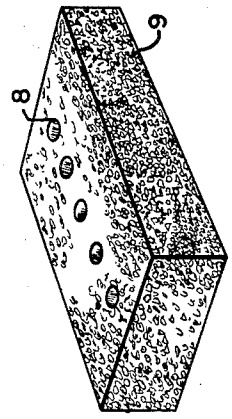


FIG.-2

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PROCESS FOR PRODUCING POROUS OIL SHALE PRODUCTS

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3 Claims. (Cl. 106—40)

This invention relates to building materials and more particularly to porous building materials such as bricks, slabs, boards, tiles and the like derived from oil bearing shales.

The production of oil from shale has increased in importance in this country in recent years and is rapidly becoming a more important factor in the utilization and conservation of our vitally necessary oil resources. The production of oil from shale has not yet attained appropriate stature due primarily to the economics of the process; one important factor is that only about 20–30% of the natural shale is convertible, the remainder having no utility under present processes. An important object this invention is the provision of a process which utilizes the material hitherto wasted.

A primary object of this invention is the provision of products from the spent shale or shale waste, which products have a high degree of saleability in present markets and will accordingly render commercially feasible the production of oil from the shale also.

The shales most suitable for the practices of the invention occur in abundance, are relatively low grade and are typified by Colorado oil shales (mahogany ledge) which are readily ground to a fine mesh; these shales contain 8–20% by weight of volatile constituents and accordingly 92–80% ash which ash may have the following composition range:

	Weight percent on fresh shale
SiO_2	39–46
Al_2O_3	10–14
CaO	20–33
MgO	8–14
Fe_2O_3	3– 5
Na_2O	1– 4
SO_3	1– 4
K_2O	1– 3

This invention contemplates that the hard, oil bearing shale will be ground to a suitable mesh, shaped to the form of a desired article of manufacture, pressured to compact the particles and then fired; the firing may be effected under such conditions that the carbonaceous matter is distilled from the article without deformation thereof.

Where desired a binder material may be incorporated in the ground oil shale prior to the molding thereof. Such binder should be selected to be without substantial effect on the carbonaceous matter of the oil shale and to not interfere with the evolution of the carbon bearing compounds from the shale in the course of firing. Such materials include sodium silicate and Portland cement in amounts of between about 5–15% by weight of the shale.

The invention will be more fully understood by reference to the following detailed description and accompanying drawing wherein:

Figure 1 is a schematic view of apparatus useful in the practice of the invention;

Figure 2 is a perspective view of an article of manufacture in the form of a porous rigid building material structure produced in accordance with the process of invention; and

Figure 3 is a view of press apparatus useful in the shaping of articles of manufacture.

Referring to the drawing and first particularly to Figure 3 there is shown at 1 a press, actuated hydraulically or by other suitable means having a lower platen 3 and an upper platen 5. Ram 7 is actuable to bring the platens toward each other to apply a suitable pressure as 100 pounds per square inch to the material 9 in the cavities of mold 11 to shape the material to a brick-like form.

The material in mold 11 is first prepared by grinding a shale the ash of which shale preferably conforms substantially to the range of formulations set out hereinbefore; the shales vary slightly in hardness and while they may usually be ground dry steaming of the shale prior to grinding facilitates the operation. Steaming where employed may be effected on suitable screens which retain the broken rock-like shale pieces and permit the steam to be passed upwardly therethrough.

Grinding to a particle size in the range of 20–100 microns is readily achieved in the dry state with most shales; this dry powdery material may then be simply placed in the various cavities of mould 11, the press closed and the material formed to brick-like shape; heat of up to about 212° F. may be utilized although not generally required since the original waxy shale is relatively free of moisture.

The application of heat at the pressing operation is usually beneficial however if the shale has been subjected to steaming prior to or during grinding.

As shown in Figure 1 a kiln 13 having metal framework 14 and a lining 15 of firebrick is provided with tracks 17; trucks 19 may be employed to carry the shale formed at the press into the kiln. The kiln is provided with doors 21, 23 and gaskets 27, 29 which may be carried on the doors; the doors have secured thereto at their upper ends cables as cable 36 which cable is operable over pulley 32 in guide 30 to raise the door 23; bolt means 25 are effective to compress the gasket in the closed position of the door to insure of air tight sealing of the kiln.

The kiln is also provided with conduits 33, 35. Conduit 33 has the exterior end thereof connecting with a suitable supply 34 of an inert gas such as CO_2; valve 37 is conveniently provided to control the CO_2 flow to the kiln.

Conduit 35 is provided with a valve 40 and a suitable condensing tower 41 for the recovery of volatiles passing outwardly of the kiln; if desired this tower may suitably have refining apparatus associated therewith for the further processing of the volatiles or the condensing tower may be replaced by such refining apparatus.

A third conduit 43 communicates with conduit 35 and is itself provided with valve 45. The remote end of conduit 43 is connected to a vacuum pump 47 for effecting exhaustion of kiln 13. Valve 46 may be suitably provided to close off both the condenser and pump from the kiln.

The kiln 13 is mounted on incombustible supports 49, which are preferably of concrete, and the underside of the kiln is adapted to be heated by gas flame 51 emanating from burner 53 to temperatures of about 2500° F.–2800° F. To resist these temperatures the bearings for the wheels of trucks 19 are sealed in.

In the practice of the process of the invention the ground material molded as indicated in Figure 3 is placed in suitable arrangement on trucks 19; the cover door 23

is opened, the track portions **26** are lowered into position to meet with track **17** at the exterior of the kiln, and the trucks roll in on the tracks. Thereafter with the doors **21, 23** each lowered and the gaskets secured valve **40** is closed, valves **37, 45** and **46** are open, and the vacuum pump **47** is operated to draw carbon dioxide from the source **34** through the kiln **13**. The CO_2 assists in the evacuation of all air from the chamber and the kiln itself may be heating during this evacuation though the temperature of volatilization of the hydrocarbons is preferably not approached until all air is evacuated. The pump and the flow of CO_2 should continue for a sufficiently long time to insure that all air has been evacuated from the apparatus; valve **37** is then shut off and the pump **47** is operated to reduce the pressure in the kiln to a very low value of CO_2

As noted during this period the kiln may be heating but should not generally be above about 1000° F. Thereafter with valves **37** and **45** closed and valves **40** and **46** open the temperature is raised to about 1800° F. The volatiles of the shale will distill off between about 1500° F. and 1800° F. and will be passed to condenser **41** or refining apparatus as desired.

With most shales substantially complete volatilization of the hydrocarbons will have taken place upon heating for about 4 hours at temperatures of about 1800° F. The time will vary somewhat with the manner in which the bricks are formed and positioned in the kiln, the various production factors in such an operation are well known and need not be considered in detail it being sufficient to state that generally at least about ½ hour will be required to insure of volatilization under high vacuum conditions at 1800° F. After evacuation valves **46** and **40** are closed and the temperature within the kiln is raised to about 2000° F. to complete firing of the shale material to porous brick. This temperature varies somewhat with the particular shale and is most affected by the alkali content thereof; the temperature must of course be maintained below the softening point of the shale residue brick.

Upon the completion of firing and with the temperature still high valve **37** may be opened to introduce a pressure of carbon dioxide (valves **40** and **46** being closed) to permit the end doors **21, 23** of the kiln to be opened. This requires that valve **37** be open only for a short period and it is closed before the doors themselves are raised. Alternatively other means may be provided for the breaking of the vacuum within the chamber to permit the end doors to be opened. The trucks **19** from within the kiln are then moved leftwardly as shown in Figure 1 and other trucks are moved into the kiln, the doors closed and the process repeated.

Between operations the intensity of the flame **51** may be reduced, but in general it will not be found necessary to discontinue heating entirely as the entrance of air and the new charge is sufficient to materially cool the kiln. It is to be noted in this connection that the volatile hydrocarbons may be cycled to a supply to be utilized in the kiln heating if desired; in such cases the hydrocarbons are preferably treated to remove lower boiling constituents prior to combustion.

The product of the operation is illustrated in Figure 2 and is a porous material, the pores being relatively small, the brick being of a very homogeneous grainless structure due to the fact that the hydrocarbons themselves are substantially uniformly dispersed in the natural shale. Such bricks or similarly other blocks, slabs, panels or tiles of the same material may be subjected to machining operations, are absorbent, and find utility particularly as building materials.

As set out hereinbefore the ground material prior to subjection to the distillation operation and prior to the compaction thereof may have mixed with it small amounts of other material such as 5–15 percent by weight of sodium silicate or Portland cement. Where a sodium silicate solution is employed the ratio of SiO_2 to N_2O should not exceed 4:1 to avoid brittleness in the product. The sodium silicate during the firing will tend to permeate the shale mass and to be adsorbed thereby resulting in good adhesion of the particles.

The Portland cement which in slurry form is mixed with the oil shale itself normally sets hard and this characteristic is reflected in the product—tending to make the porous shale residue brick hard and very inflexible. A clay slurry may also be employed and in fact the clay may in some cases be predominant, the oil shale being introduced to provide on firing of the clay a porous structure.

It is generally desired to heat platen **3** or press **1** to permit excess water to be removed at the pressing stage. The pores of the product will in general be somewhat larger when an aqueous slurry of Portland cement or of the silicate is employed due to the volatilization of the water during the early stages of the distillation operation.

It is to be noted in this latter respect that where water is incorporated into the ground shale mass valve **40** is not opened until the water is completely driven off which will normally be at a temperature considerably less than 250° F., the water being evacuated through the pump **47**. Such procedure requires that the kiln be permitted to cool materially between operations and always it is necessary to complete evacuating the interior of the kiln of water, oxygen, etc. before raising the temperature above 1500° F.

The product, when water is incorporated into the shale mass, is subject to somewhat greater shrinkage during the processing and accordingly the pores will tend to become somewhat closed by the shrinkage. The porosity always is greater than 10% of the volume and normally, depending upon the volatile content of the shale, the voids exceed 20% by volume of the article.

The product, whether it has a binder incorporated therein or not, is of relatively light weight, suitable for all general building material conditions requiring rigid structures and may be ornamented or painted in much the same manner as ordinary clay bricks.

It is further to be noted that the product of invention, the chemical constitution of which corresponds to the ash of the original shale, may be attained by firing the bricks or other articles without care to the preservation of the hydrocarbons. Such procedure is economically without merit presently however.

It will be understood that this invention is susceptible to modification in order to adopt it to different usages and conditions and accordingly, it is desired to comprehend such modifications within this invention as may fall within the scope of the appended claims.

I claim:

1. In a process of producing a porous, non-brittle, homogeneous, grainless building material structure the steps of: (*a*) grinding oil shale to a particle size in the range of about 20–100 microns; (*b*) compressing the particles of oil shale with a sodium silicate binder while heating the same to form a brick-like body; (*c*) evacuating and heating a closed spacing with the brick-like body therein; (*d*) flushing the spacing with carbon dioxide; (*e*) raising the temperature within the spacing sufficiently to distill off volatiles of the formed body of the shale; and (*f*) sintering the material after completion of the distillation.

2. In a process of producing a porous, non-brittle, homogeneous, grainless building material structure, the steps of: (*a*) grinding oil shale to a particle size in the range of about 20–100 microns; (*b*) compressing the particles of oil shale with a binder selected from the group consisting of sodium silicate and Portland cement while heaating the same to form a brick-like body; (*c*) evacuating and heating a closed spacing with the brick-like body therein; (*d*) flushing the spacing with a non-oxidizing gas to evacuate all air from the spacing; (*e*)

raising the temperature within the spacing sufficiently to distill off volatiles of the formed body of the shale; and (*f*) sintering the material after completion of the distillation.

3. In a process of producing a porous, non-brittle, homogeneous, grainless building material structure, the steps of (*a*) grinding oil shale to a particle size in the range of about 20–100 microns; (*b*) compressing the particles of oil shale with a binder selected from the group consisting of sodium silicate and Portland cement while heating the same to form a brick-like body; (*c*) evacuating and heating a closed spacing with the brick-like body therein; (*d*) flushing the spacing with carbon dioxide; (*e*) raising the temperature within the spacing sufficiently to distill off volatiles of the formed body of the shale; and (*f*) sintering the material after completion of the distillation.

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