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MANUFACTURE OF CARBURIZED SILICA

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Fig. 1.

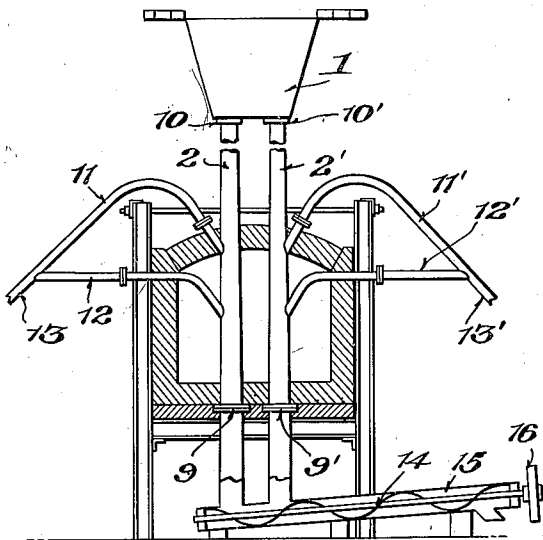


Fig. 2.

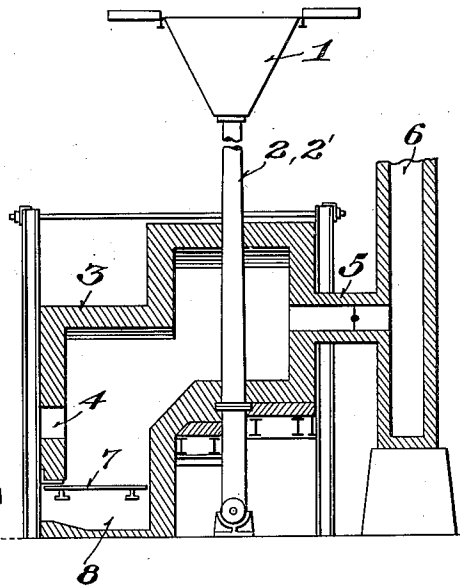
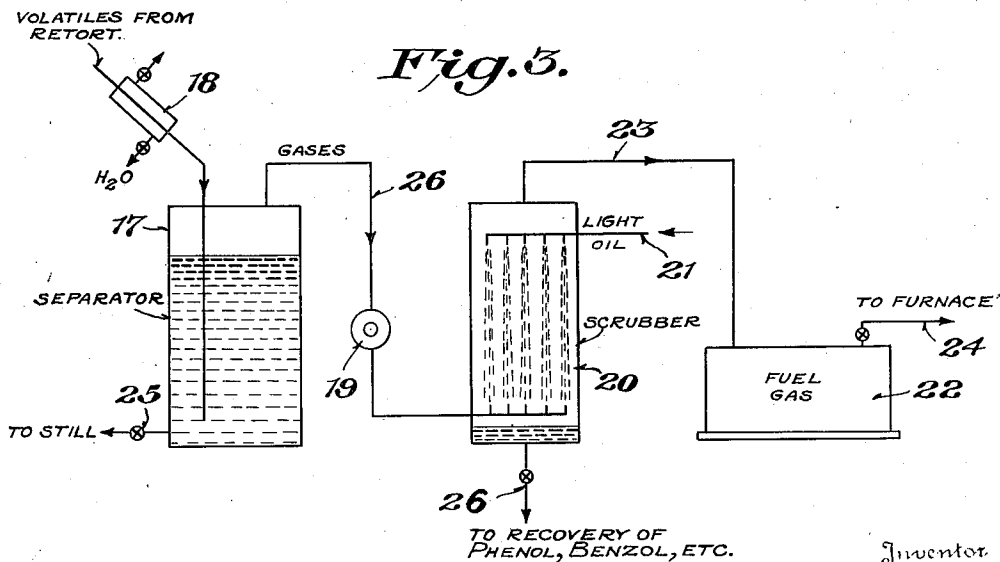


Fig. 3.



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MANUFACTURE OF CARBURIZED SILICA

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5 Claims. (Cl. 196—50)

My invention relates to manufacture of carburized silica; and it comprises a process wherein a tar of the nature of coal tar is intimately mixed with a finely divided siliceous product of the nature of diatomaceous earth, said mixture is passed continuously through a reaction zone wherein it is subjected to a destructive distillation and the resulting solid product is continuously withdrawn; the vapors formed in the process are partially condensed, the condensate being subjected to a fractional distillation for the recovery of various products, the remaining vapors are scrubbed with a light oil to remove other valuable products and the remaining gases are then recovered; all as more fully hereinafter set forth and as claimed.

It has hitherto been proposed to prepare a carburized silica product by submitting to destructive distillation a mixture of a carbonaceous substance, such as coal, and a siliceous substance, such as diatomaceous earth. Such a process is described in my prior U. S. Patent No. 1,940,352. I have called this product "Silica Black". When employing a carbonaceous material such as coal, however, a larger amount of ash is carried along with the silica black products which tends to discolor the same and to give a product of varying texture. The product, while very useful, is not as uniform and of as high a quality as is required in some industries.

I have found that the use of a tar of the nature of coal tar instead of coal obviates these difficulties, giving a jet-black, even-textured carburized silica. I have found that coal tar is an ideal starting material for a process of this character both for procedural and economic reasons. The use of tar in this process likewise provides for the recovery of all the valuable distillates as by-products of the process. I have also improved my prior process by the development of a continuous method which produces a better product with a substantial reduction in over-all cost.

I have made the further discovery that when coal tar is destructively distilled with diatomaceous earth or other siliceous material of like nature the latter acts as a catalyst and the coal tar is catalytically decomposed. This catalytic decomposition of the coal tar results in the production of increased amounts of phenol, cresol and mixed hydrocarbons and nearly twice the normal amounts of naphthalene, anthracene and phenanthrene. In addition to these products, there is produced some anthraquinone which, I have found, can be separated easily. This last-mentioned product is not obtained in the ordinary

distillation of coal tar but is generated, presumably, by the catalytic oxidation of anthracene in my process. Furthermore, large volumes of a rich combustible gas are obtained which may be utilized in this or other arts.

Broadly stated the present invention contemplates the continuous destructive distillation of coal or other tar of like nature in intimate admixture with finely divided diatomaceous earth, or other siliceous material of like nature, such as infusorial earth, in such manner that there is obtained a carburized silica of greatly improved texture, coloring power, etc., along with the products of the destructive distillation of tar.

In order that my process may be explained in greater detail reference is made to the accompanying drawing which shows, more or less diagrammatically, an advantageous form of apparatus for carrying out my said process. In this showing:

Fig. 1 is a front elevation of my retort with the furnace in section,

Fig. 2 is a section along the lines 2—2 of Fig. 1, while

Fig. 3 is a diagrammatic showing of one method of treating the volatile products obtained in my process.

In my process, wherein use is made of the apparatus shown in Figs. 1 and 2 an intimate mixture is first made of coal tar and finely divided diatomaceous earth or other siliceous substance, preferably in the ratio of about 80 parts of tar to 100 parts of diatomaceous earth, by weight. Mixing may be accomplished, for example, in a device (not shown) wherein a weighed amount of molten tar is poured or sprayed upon an agitated weighed mass of diatomaceous earth, taking care to maintain the mixture in a powdered state during mixing.

The powdered mixture of tar and siliceous material is conveyed to the hopper 1 from which it is allowed to fall into the long, vertically disposed retort pipes 2, 2', of which there may be any desired number and which are constructed of any suitable heat resistant alloy. These pipes pass through the furnace, generally designated at 3. The furnace is maintained at substantially an orange red to yellow heat (700° to 1200° C.) by combustion of any suitable fuel fed through door 4, the hot gases passing upwardly and around retort pipes 2, 2' and then through conduit 5 and flue 6. When solid fuel is used in the furnace the latter is provided with a grate 7 and ash pit 8. It is, of course, understood that I contemplate the use of any suitable fuel, solid, liquid or gaseous.

As a matter of fact, the fuel gas by-product of my process, may be utilized for this purpose, if desired.

The retort pipes 2, 2' are supported by flanges 9, 9' in the lower layer of the furnace and also by flanges 10, 10' mounted in the base of the hopper 1. In order to prevent clogging of the mixture passing through the retort pipes, their cross section may be increased slightly downwardly, the diameter at the bottom being of the order of two inches larger than that at the top.

In passing through the retort pipes 2, 2' the tar of the mixture is catalytically decomposed and destructively distilled at the temperature maintained in the furnace, all of the volatile products being allowed to pass out of the retort pipes into condenser pipes 11, 11' and 12, 12'. These condenser pipes, arranged on either side of the furnace, terminate in common conduits 13, 13', respectively, which in turn may lead to a condenser 18 then to a separatory chamber 17 (Fig. 3) of suitable size and shape for the collection of the liquid distillate.

The rate of flow or drop of the distilling mixture in the retort pipes 2, 2' is regulated by the speed of the screw conveyor 14 located in discharge pipe 15 and driven by any suitable driving mechanism operating upon pulley 16.

The discharge pipe 15, which is welded to the lower ends of retort pipes 2, 2' is slightly elevated at the exit end in order to prevent air from reaching the hot carburized silica before it has had time to cool. I have found this precaution desirable because the carbon will burn out and ruin the product if exposed to air at temperatures in excess of about 450° C. It is possible, of course, to positively cool conveyor pipe 15. Or, if desired, a heat recuperator may be placed around the exit of conveyor 15 and employed for heating the air which is subsequently used for combustion purposes.

The volatile products obtained in my process, which pass from the retorts 2, 2' by means of pipes 13, 13' may be treated in various ways. The vapor pipes 13, 13' may be water cooled, if desired, as shown at 18 in Fig. 3, before passing to separator 17. The gases leaving separator 17 by pipe 26 are advantageously passed through a pump 19 which produces a slightly sub-atmospheric pressure in a small section of the retort tubes 2, 2'. This reduced pressure prevents loss of volatiles from hopper 1. The gases leaving pump 19 are passed through a scrubber 20 which is fed by a light oil through line 21. The scrubbed gases then pass into fuel gas receiver 22 by line 23. These gases may then leave by line 24 to be used in heating the furnace 3. I have found that my process, conducted as described, roughly yields from about 4500 to 5500 cubic feet of rich fuel gas for each ton of tar processed.

The separator 17 is usually maintained at a temperature ranging from about 20° to 50° C. The liquid products collecting in this separator are drawn off by pipe 25. These products may be fractionated by conventional methods. The first fraction recovered, which is usually taken off when the temperature reaches about 125° C. contains a large amount of water and a light oil. The oil can be readily separated and may be used to make a paint, as described subsequently. The aqueous solution remaining is alkaline and contains ammonia, pyridine and other basic constituents, which may be recovered by standard methods.

The second fraction, usually taken off at tem-

peratures ranging from about 175° to 225° C., is found to contain naphthalene, cresylic acid and phenol. These products can be separated and recovered by conventional methods. The third fraction, usually taken off at temperatures ranging from 225° to 300° C. contains anthracene oil from which crude anthracene can be separated on standing.

The fourth fraction taken off at temperatures ranging from about 300° to 400° C. is a greenish solid product dispersed in a heavy hydrocarbon oil. If this solid product is extracted with hot alcohol and the solution filtered it will be found that the filtrate contains anthracene while crude anthraquinone is retained on the filter. A small amount of phenanthrene is also present in this fraction and can be recovered if desired.

A fifth fraction may be recovered if desired at temperatures ranging from about 400° to 500° C., this fraction being a mixture of high molecular weight hydrocarbons in liquid form. Unless the temperature has gone to carbonization, a pitch remains in the retort which may be dissolved in the light oils obtained in the first fractions. This solution, to which silica black is added makes a superior paint, that is not only waterproof and rust resistant but withstands unusually high temperatures. For dissolving the pitch, benzol or other light oils may be used.

Before the above described fractionation of the distillate from 17 is undertaken, it may be desirable to first carry out a steam distillation of it, in which case the water layer will contain ammonia, pyridine, some phenol and other basic constituents. A fractionation of the oil layer will result in products very similar to those described above.

The scrubbing oil drawn off from the bottom of scrubber 20 by pipe 26 contains benzol, etc., which may be recovered by conventional methods, the oil used as a scrubbing liquid being then returned to the process. The light oil obtained in the first fraction, as described above, may be used as scrubbing liquid in the scrubber 20, if desired. It is advantageous to employ an oil from which the products can be separated readily by distillation.

I find that, generally speaking, optimum conditions are obtained when the temperatures at the circumference of the retort pipes is maintained at from about 700° to 1200° C. The temperature at the center of the pipes will the range from about 450° to 900° C. Although it will be understood that this latter range is dependent upon the rate of flow of material through the pipes, which rate of flow will be determined by the nature of the product, most desired.

For the production of a given product the rate of flow in the tubes varies directly with the temperature to which the tubes are heated. At very low rates of flow the furnace temperature may drop two to three hundred degrees, for example. The time of heating may vary from about 10 to 60 minutes.

After cooling, the silica black resulting from my process is preferably classified into at least two portions by air flotation in a manner illustrated in my prior acknowledged patent. The lighter portion may serve as an excellent black pigment, as a body for an acid proof or rust-proof paint, an insecticide carrier or as a carrier for catalysts, while the heavier portion is found to be particularly useful as an absorbent for gases, as a filtering medium and as a filler or pigment for hydraulic and other cements.

The finished products are comparatively soft

powders, jet black in color and unusually uniform in texture. The analysis of typical samples is as follows:

	Finest air floated	Heavier air floated
	Percent	Percent
Silica (SiO ₂).....	72.5	70.3
Carbon.....	21.1	23.0
Non-siliceous inorganic residue.....	6.4	6.7

The apparent specific gravity of the lighter grade is approximately 0.215 while that of the heavier grade is 0.409.

While I have described what I consider to be the most advantageous embodiment of my process, various modifications can be made therein without departing from the scope of the present invention. All types of true tars can be employed in my process, that is, tars of the nature of coal tar. The process illustrated diagrammatically in Fig. 3 can, of course, be varied widely in order to recover the various valuable products produced in my process. If desired the liquid products collected in separator 17 may be steam distilled to recover low boiling fractions, followed by vacuum distillation to prevent destruction of the heavier oils which are obtained in the process. The proportions of tar used in my process may vary from about 50 to 100 parts for 100 parts of siliceous material. Other modifications which fall within the scope of the following claims will be immediately evident to those skilled in the art.

What I claim is:

1. A process for preparing a soft uniformly colored and textured carburized silica product which comprises intimately mixing coal tar with finely divided diatomaceous earth in the proportions of from about 50 to 100 parts of tar to 100 parts of diatomaceous earth, passing the mixture continuously through a reaction zone in the absence of air while controlling the temperature and time of passage through said reaction zone in such manner as to destructively distill the coal tar while carbonizing the residual tar, recovering condensates from the volatiles derived from said process and also recovering the carburized silica product.
2. The process of claim 1 wherein the mixture in the reaction zone is heated within the temperature range of from about 450° to 900° C.
3. The process of claim 1 wherein the coal tar and diatomaceous earth are mixed in the proportions of about 80 parts of tar to 100 parts of diatomaceous earth.
4. The process of claim 1 wherein said volatiles are partially condensed and the remaining vapors are scrubbed with a light oil.
5. The process of claim 1 wherein said mixture is passed in a body downwardly through said reaction zone by gravity, the resulting solid carburized silica product being continuously removed at the bottom of said reaction zone and said mixture being added at the top of said zone to maintain a body of reacting material in said zone.

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